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GEOPHYSICAL RESEARCH PAPERS

NO. 39

THE CHEMISTRY AND VERTICAL DISTRIBUTION  
OF THE OXIDES OF NITROGEN  
IN THE ATMOSPHERE

LEWIS E. MILLER

NOVEMBER 1954

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GEOPHYSICS RESEARCH DIRECTORATE  
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## FOREWORD

The temperature of the earth's atmosphere is considered to be governed largely by the equilibrium between absorbed and emitted radiation. Thus, the radiation passing through the stratosphere has been shown to consist (a) of that from the sun chiefly of the wavelength interval 0.4 to  $2\mu$  (4000-20,000 Å), and (b) that from the earth and lower layers of the atmosphere of the wavelength region 4 to  $10\mu$ . Strangely enough the main constituents of the atmosphere in abundance are practically transparent to radiations in the above wavelengths. The absorption in the atmosphere depends upon the presence of the minor constituents of the air, such as water vapor, carbon dioxide, ozone and various oxides of nitrogen. A striking feature is the great intensity and complex structure of the absorption spectra in the infrared and ultraviolet shown by nitrous oxide, ozone, water vapor and carbon dioxide.

The absorption bands of these minor gaseous components of the atmosphere in the solar spectrum have been most widely employed to detect and measure their distribution. Knowledge of the abundance and vertical distribution of these gases is important, since such data provide useful information on the temperature balance of the atmosphere. Evidence from the spectra of the auroral light, which is emitted by strong excitation of the air particles caused by fast moving corpuscles coming from the sun, seems to indicate that everywhere up to 600 km, at least, the atmosphere is a nitrogen-oxygen atmosphere.

Nitrous oxide is the only oxide of nitrogen whose presence in the atmosphere has been established by direct observational evidence to exist, for a certainty, in the upper atmosphere. All three fundamentals,  $\nu_1$  at  $7.8\mu$ ,  $\nu_2$  at  $17.0\mu$  and  $\nu_3$  at  $4.5\mu$ , of nitrous oxide have now been identified in the telluric spectrum. Prior to the discovery of nitrous oxide in the upper atmosphere many investigations in the laboratory yielded valuable information on its absorption spectra in the infrared, ultraviolet and vacuum ultraviolet spectral regions.

Brief summaries of these early papers as well as more recent experimental laboratory studies on the photolysis and thermal decomposition of nitrous oxide, nitric oxide, and other oxides of nitrogen have been included in this paper. These abstracts, or summaries, have been arranged chronologically and alphabetically within each year. They have been grouped as (a) nitrous oxide, (b) nitric oxide and (c) nitrogen dioxide and other oxides of nitrogen.

Several papers of a theoretical nature have considered certain homogeneous gas reaction mechanisms for the distribution of the nitrogen oxides in the upper atmosphere. At altitudes of the spectacular auroral phenomena the present day picture of the atmosphere at these heights is that the air consists largely of atomic oxygen, molecular nitrogen, and atomic nitrogen. Molecular oxygen predominates below about 100 km and atomic oxygen above this altitude. Some investigators have reported evidence for N II emission lines; the existence of O II emission lines are less certain. Homogeneous gas reactions among these atmospheric constituents appear probable and lend themselves to many interesting speculations about the production of the various oxides of nitrogen in the atmosphere, as well as their photodissociation and recombination processes in the upper atmosphere. There is also supporting evidence that photoionization of nitric oxide may be an important mechanism in the formation of the D layer.

Recently, investigations on the photochemistry in the lower atmosphere at ground level have yielded information of immense practical significance. Nitrogen dioxide ( $\text{NO}_2$ ), while not considered an important oxide of nitrogen in the upper atmosphere, is regarded as the most prevalent of the oxides of nitrogen in air pollution and during periods of intense smog conditions. It has been estimated that the exhaust fumes from approximately 2,000,000 automobiles, trucks, busses, and other motor vehicles in the country with an average daily mileage of about 50,000,000 miles contribute about 40 tons of nitrogen oxides into the atmosphere. Although the concentration of the oxides of nitrogen does not reach toxic levels in the atmosphere, their catalytic action in the presence of sunlight in photochemical reactions leading to the formation of atmospheric ozone and many organic peroxides, oxidants which characterize smog effects, has been demonstrated by extensive studies.

It is probably safe to conclude that laboratory investigations on the oxides of nitrogen, which might appear to be theoretical in nature, upon absorption coefficients, absorption and photoionization cross sections, and photochemistry have many times in the past proved to be of most practical and economic consequence. The oxides of nitrogen have played an important role in the study of chemical kinetics. There are yet many photochemical processes involving the oxides of nitrogen not fully understood. A knowledge of them can lead to a better understanding of our atmosphere.

LEWIS E. MILLER

Atmospheric Standards Section  
Atmospheric Physics Laboratory

# THE CHEMISTRY AND VERTICAL DISTRIBUTION OF THE OXIDES OF NITROGEN IN THE ATMOSPHERE

## 1. SUMMARY AND EVALUATION

### 1.1 INTRODUCTION

One of the main problems in the study of the composition of the upper atmosphere is the distribution, abundance and pressures of the constituent gases. In order to carry out calculations it is necessary to know approximately the height at which photochemical decomposition, formation and photoionization of the atmospheric gases under the action of solar radiations begin to be important. The composition of the earth's atmosphere is essentially an oxygen-nitrogen atmosphere. In the following table by Paneth, it may be observed that 98.95 percent by volume is due to nitrogen and oxygen, 0.93 percent argon and 0.03 percent carbon dioxide, leaving a remainder of about 0.09 percent for the inert gases, ozone, oxides of nitrogen and other minor atmospheric constituents.

Table I. Composition of the Atmosphere up to About 60 km

Constituent	Percent by Volume	Reduced Thickness (atmo-cm NTP)
Nitrogen	78.09	625,000
Oxygen	20.95	168,000
Argon	0.93	7,440
Carbon dioxide	0.03	240
Neon	$1.8 \times 10^{-5}$	14.6
Helium	$5.24 \times 10^{-4}$	4.2
Krypton	$1 \times 10^{-4}$	0.8
Hydrogen	$5 \times 10^{-5}$	0.4
Xenon	$8 \times 10^{-6}$	0.06
Radon	$6 \times 10^{-18}$ (variable decreasing with height)	

Note: The above values are given for dry air.

From F. A. Paneth, *Quart. J. Meteor. Soc.* 63, 433 (1937). Ibid. 65, 304 (1939).

Table II. Minor Constituents of the Atmosphere

Constituent	Percent by Volume	Reduced Thickness (atmo-cm NTP)
Water vapor	0.1-2.8	0.25 mm-50 mm liquid water
Ozone	$1 \times 10^{-8}$	0.3
Nitrous oxide	$5 \times 10^{-8}$	0.4
Methane	$1.4 \times 10^{-4}$	1.2
Carbon monoxide	$1 \times 10^{-4}$	0.09-0.4
Heavy water	$10^{-8}$ of water vapor	

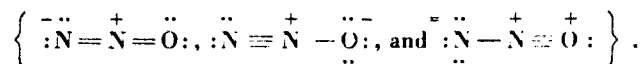
Miller, L. E., *J. Chem. Ed.* 31, 112-124 (1954).

It is the purpose of this survey to examine the evidences in the literature for the occurrence, origin, vertical distribution and abundance of atmospheric nitrous oxide and the other oxides of nitrogen. The oxides of nitrogen are to be expected as combustion products in industrial areas, and have been found in the atmosphere over large cities in concentrations comparable to those found for sulfur dioxide. They are considered of importance in meteorological phenomena, and are therefore of interest to study from a practical viewpoint as well as their place in geophysics and astrophysics, in ionospheric phenomena, the aurorae and the night airglow.

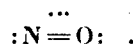
## 1.2 ELECTRONIC STRUCTURE

Most of the molecules of the oxides of nitrogen are resonance hybrids. The various single and double bonds may change places. The most stable ones are nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>). They are "odd" molecules, i.e., they contain an odd number of electrons. These two oxides of nitrogen represent oxidation levels for nitrogen not usually occurring in other of its compounds. The resonance of the odd electron, according to theory, between the two or three atoms of the molecule appears to stabilize the substances NO and NO<sub>2</sub>.

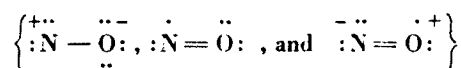
*Nitrous oxide* (N<sub>2</sub>O) has a linear molecule, and its electric dipole moment is practically zero. The linear and non-symmetrical character of the molecule of N<sub>2</sub>O was established by Plyler and Barker (*Phys. Rev.* 38, 1827 (1931)) from infrared spectroscopic data and rotational analysis of the N<sub>2</sub>O bands at 17.0 μ, 7.78 μ and 8.6 μ under high dispersion. The structure was later confirmed by Schomaker and Spurr (*J. Am. Chem. Soc.* 64, 1184 (1942)) by the electron diffraction method. The possible resonating electronic structures are:



*Nitric oxide:* The nitric oxide (NO) molecule has an odd number of electrons and is paramagnetic. Pauling has represented the molecule with a double bond and a three-electron bond as follows:

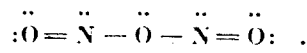


The structure is also given as a resonance hybrid.

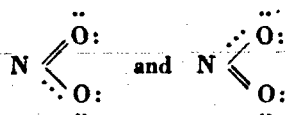


Chemically, nitric oxide is unsaturated in character, forming such compounds as the nitrosyl halides by addition, such as NOCl. The odd electron may also be lost yielding the nitrosyl (or nitrosonium) cation NO<sup>+</sup> in such well-known compounds as nitrosyl sulfuric acid, NOHSO<sub>4</sub>.

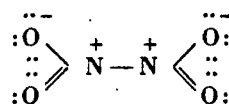
*Nitrogen sesquioxide*, or dinitrogen trioxide (N<sub>2</sub>O<sub>3</sub>), incorrectly called nitrogen trioxide, probably exists only in the solid state as a pure compound. In the vapor phase the molecule is almost completely dissociated. A solid substance which melts sharply at about -103°C is obtained by condensing and solidifying an equimolecular mixture of NO and NO<sub>2</sub>. The structure of the N<sub>2</sub>O<sub>3</sub> molecule has not been established by physical methods. Chemically it has been shown to have a probable symmetrical structure:



**Nitrogen dioxide** ( $\text{NO}_2$ ), sometimes erroneously called nitrogen peroxide, is an "odd" molecule and is paramagnetic. The structure was deduced by Sutherland and Penny (*Nature* 136, 146 (1935)) to be non-linear. The electronic structure is not known for a certainty. According to Pauling the structure resonates between

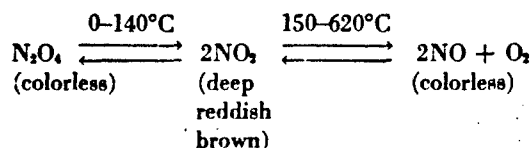


**Nitrogen tetroxide** ( $\text{N}_2\text{O}_4$ ) or dinitrogen tetroxide: Although the structure of  $\text{N}_2\text{O}_4$  is not known with certainty, Hendricks (*Z. Phys.* 70, 699 (1931)), Sutherland (*Proc. Roy. Soc. (London)* A 141, 343 (1933)), and Giauque and Kemp (*J. Chem. Phys.* 6, 40 (1938)) have suggested a symmetrical structure

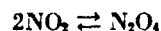


from X-ray measurements on the solid, by spectroscopic studies of the infrared and Raman spectra, and thermodynamic properties.

The composition of nitrogen dioxide and its dimer,  $\text{N}_2\text{O}_4$ , may be best expressed by the following equilibria:

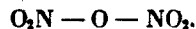


Liquid  $\text{NO}_2$  is largely polymerized to nitrogen tetroxide,  $\text{N}_2\text{O}_4$ . At the boiling point about 20 percent of the tetroxide is dissociated into the dioxide. Upon cooling the color of the liquid becomes lighter in color, and freezes at  $-11.2^\circ\text{C}$  to a colorless solid which is pure  $\text{N}_2\text{O}_4$ . Between  $130-140^\circ\text{C}$  the dissociation into  $\text{NO}_2$  is practically complete. At higher temperatures the  $\text{NO}_2$  further dissociates into  $\text{NO}$  and  $\text{O}_2$ , becoming completely dissociated at about  $620^\circ\text{C}$ . The equilibrium constant for the reaction:



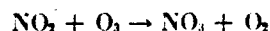
is 8.8. At  $25^\circ\text{C}$  the equilibrium mixture is largely  $\text{N}_2\text{O}_4$ .

**Nitrogen pentoxide** ( $\text{N}_2\text{O}_5$ ) in the solid state has a crystalline lattice structure containing the ions,  $\text{NO}_2^+$  and  $\text{NO}_3^-$  with distances of 1.15 and 1.24 Å, respectively. Nitrogen pentoxide is a colorless solid which sublimates without melting. At temperatures above  $0^\circ\text{C}$  it begins to dissociate into  $\text{N}_2\text{O}_4$  and  $\text{O}_2$ . In the vapor state the molecule is believed to have the structure

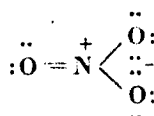


**Nitrogen trioxide** ( $\text{NO}_3$ ) has been described by Schwartz and Achenbach (*Ber.* 68, 343 (1935)) as a white solid which decomposes above  $-140^\circ\text{C}$  into  $\text{NO}_2$  and  $\text{O}_2$ . New bands in the absorption spectrum of ozone when mixed with either  $\text{NO}_2$  or  $\text{N}_2\text{O}_5$  have been observed by several investigators. Lowry and others (1936-1938) found that  $\text{N}_2\text{O}_5$  vapor when mixed with a small amount of ozone produced a blue gas which decomposed with luminescence at  $100^\circ\text{C}$ . Nitrogen trioxide in the gaseous phase is probably formed under these conditions.

Klemenc and Neumann (*Z. anorg. Chem.* 232, 216 (1937)) have shown that it is doubtful if the white solid is obtained by exposing a mixture of  $\text{N}_2\text{O}_5$  and  $\text{O}_2$  to the electric discharge at a low temperature. Schumacher (*Z. anorg. Chem.* 233, 47 (1937)) obtained a definite concentration of  $\text{NO}_3$  by the reaction of nitrogen dioxide with ozone.

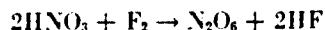


Jones and Wulf (*J. Chem. Phys.* 5, 873 (1937)) obtained spectroscopic evidence for the existence of the trioxide and showed that nitrogen trioxide,  $\text{NO}_3$ , does not contain the peroxy-linkage,  $-\text{O}-\text{O}-$ , and therefore cannot be considered to be an anhydride of peroxyntic acid,  $\text{HNO}_4$ . The structure of the molecule has been written as



with resonance between the three oxygen atoms.

Nitrogen hexoxide ( $\text{N}_2\text{O}_6$ ) is formed by the action of fluorine on nitric acid.



Its preparation has been described by Fichter and Brunner (*Helv. Chem. Acta* 12, 306 (1929)). This oxide is clearly distinct from the trioxide,  $\text{NO}_3$ , and appears to be the mixed anhydride of nitric and peroxyntic acids. The structure is probably



## 1.2 NOMENCLATURE FOR OXIDES OF NITROGEN

In the following table the systematic or stoichiometric names of the oxides of nitrogen are given. These names were recommended by the International Union of Chemistry (I.U.C. system). In this literature survey the old names of the nitrogen oxides are used, since all references in the literature about nitrous oxide and

Table III. Nomenclature of Oxides of Nitrogen

Formula	Old Name	I.U.C. Name Systematic or Stoichiometric
$\text{N}_2\text{O}$	Nitrous oxide	Dinitrogen monoxide
$\text{NO}$	Nitric oxide	Nitrogen oxide
$\text{N}_2\text{O}_3$	Nitrogen sesquioxide (Sometimes called nitrogen trioxide)	Dinitrogen trioxide
$\text{NO}_2$	Nitrogen dioxide (Erroneously called nitrogen peroxide)	Nitrogen dioxide
$\text{N}_2\text{O}_4$	Nitrogen tetroxide	Dinitrogen tetroxide
$\text{N}_2\text{O}_5$	Nitrogen pentoxide	Dinitrogen pentoxide
$\text{NO}_3$	Nitrogen trioxide	Nitrogen trioxide
$\text{N}_2\text{O}_6$	Nitrogen hexoxide	Dinitrogen hexoxide

(The prefix "mono" can generally be omitted.)

the other oxides of nitrogen in the atmosphere employed the old names. The newer nomenclature is gradually coming into usage, especially in the chemical literature. Eight oxides of nitrogen have been described in the literature, and evidence is fairly certain for their existence as pure compounds. Some have been prepared and obtained only under special conditions.

Table IV. Physical Properties of Oxides of Nitrogen

Property	N <sub>2</sub> O	NO	N <sub>2</sub> O <sub>4</sub>	NO <sub>2</sub> & N <sub>2</sub> O <sub>4</sub>	N <sub>2</sub> O <sub>5</sub>	NO <sub>2</sub>
Color	Colorless	Colorless	Blue	Reddish-brown	Colorless	Bluish Gas
F.P. °C	-102.4	-163.61	-102	-11.2	41	
B.P. °C	-88.5	-151.74	3.5	21.3	32.5 (subl.)	
Solubility in H <sub>2</sub> O, 0°C						
In 100 parts per Vol.	130.52 cm <sup>3</sup>	7.34 cm <sup>3</sup>	Soluble	Soluble, decomp.	Soluble	Soluble
Density	1.977 g/L	1.3402 g/L	1.447 <sup>a</sup>	1.491 <sup>a</sup>	1.642 <sup>b</sup>	
ΔH° kcal/mol	19.49	21.600	20.0	NO <sub>2</sub> (g) 8.091 N <sub>2</sub> O <sub>4</sub> (g) 2.309		13 ca
ΔF° kcal/mol	24.76	20.719		NO <sub>2</sub> (g) 12.390 N <sub>2</sub> O <sub>4</sub> (g) 23.491	32	
S° cal/deg	52.58	50.339		NO <sub>2</sub> (g) 57.47 N <sub>2</sub> O <sub>4</sub> (g) 72.73	27.1	
Trouton Constant	21.4	27.1		30.9		
Bond distance	N - O 1.19 Å N - N 1.12 Å	N - O 1.14 Å		NO <sub>2</sub> N - O 1.20 Å N <sub>2</sub> O <sub>4</sub> N - N 1.64 Å N - O 1.17 Å	N - O 1.15 Å in NO <sub>2</sub> <sup>+</sup> ion 1.24 in NO <sub>2</sub> <sup>-</sup> ion	

#### 1.4 NITROUS OXIDE (N<sub>2</sub>O)

##### 1.4.1 Historical

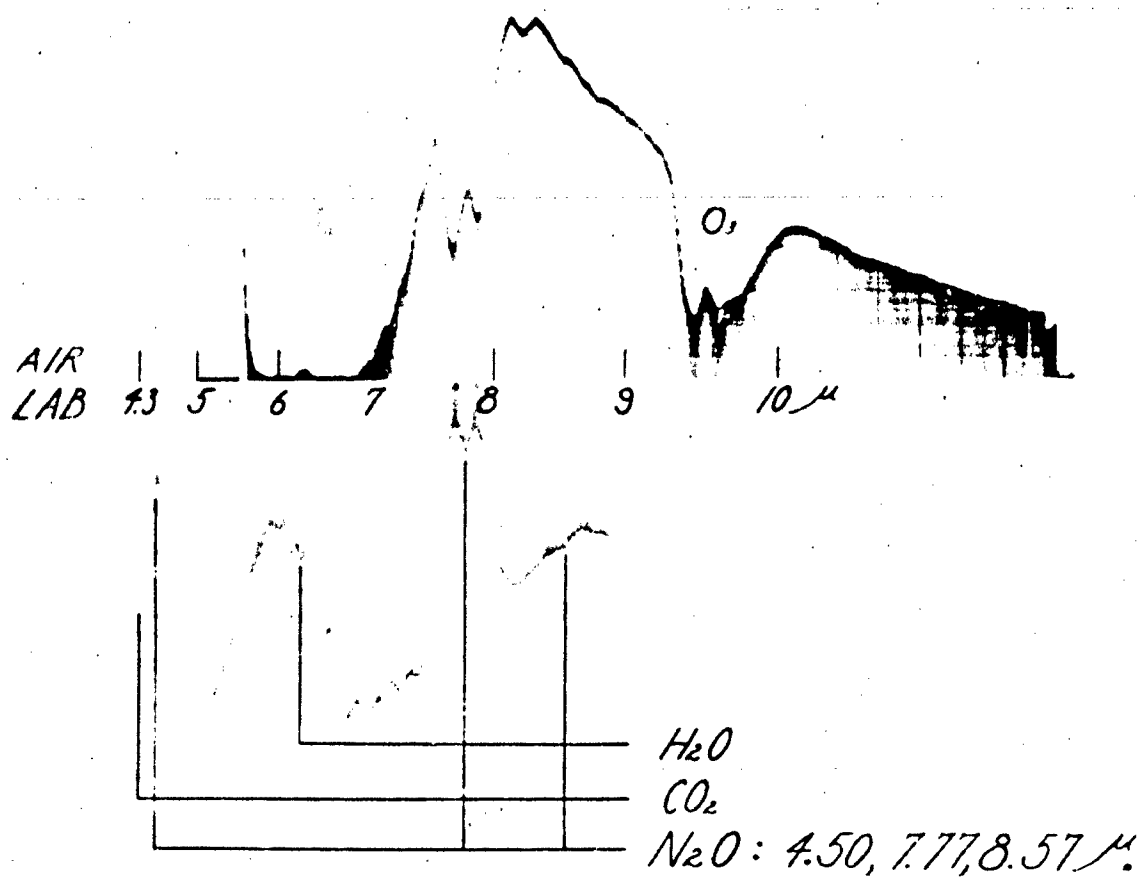
The presence of nitrous oxide as a world-wide permanent constituent in the earth's atmosphere was first observed by Adel (1939) from infrared spectroscopic evidence of the  $\nu_1$  fundamental at  $7.8\mu$  in the solar spectrum. Later the presence of atmospheric nitrous oxide was confirmed by observational bands at  $3.9\mu$ ,  $4.5\mu$  and  $8.6\mu$  by Migeotte (1948); it was also confirmed by Shaw, Sutherland and Wormell (1948) through recognition of bands at  $3.9\mu$ ,  $4.06\mu$  and  $4.5\mu$ . Nitrous oxide is the only oxide of nitrogen whose presence in the atmosphere has been established by direct observational evidence. The absorption band of nitrous oxide in the infrared of the solar spectrum have been most widely employed to detect and measure its distribution.

##### 1.4.2 Origin of atmospheric nitrous oxide

In geophysics as in many of the other Earth and Astronomical Sciences it is always interesting to speculate about the origin of the permanent constituents of the terrestrial atmosphere. In astrophysics volumes have been written about the origin of the solar system, the origin of comets, etc. The nitrogen cycle, the oxygen and carbon dioxide cycles to account for the constancy of composition of these atmospheric constituents are well-known. With reference to the comparatively newly discovered permanent atmospheric



gas, nitrous oxide, which is remarkable in being planet-wide in distribution, and rather constant in abundance, two theories have been suggested for its occurrence in our atmosphere.



Courtesy of Arthur Adel, Lowell Observatory, Flagstaff, Arizona.

Fig. 1. Identification of atmospheric  $N_2O$  through comparison of the solar prismatic spectrum with the prismatic spectrum of a laboratory sample of  $N_2O$ . The existence of  $N_2O$  in the earth's atmosphere was established by Adel by the observation of the  $\nu_1$  fundamental absorption band of  $N_2O$  at  $7.78 \mu$  in the solar spectrum.

Table V. The Discovery, Identification and Vertical Distribution of Atmospheric Nitrous Oxide

Investigator	Date	Place	Discovery	Reference	Remarks
Adel & Lampland	1938	Arizona	Band at $7.6 \mu$ in Absorption Spectrum Earth's Atmosphere	<i>Astrophys. J.</i> 87, 198 (1938)	Attributed to hitherto unrecognized atmospheric constituent, probably $N_2O$
Adel	1938	Arizona	Bands at $7.77 \mu$ and $8.5 \mu$ studied	<i>Astrophys. J.</i> 88, 186 (1938)	The presence of atmospheric $N_2O$ indicated
Adel	1939	Arizona	The telluric Bands at $7.77 \mu$ and $8.57 \mu$ compared with laboratory spectrum of $N_2O$	<i>Astrophys. J.</i> 90, 627 (1939)	An atmospheric layer of $N_2O$ comparable to $O_3$ layer indicated, several mm thick
Adel	1941	Arizona	Rotational structure of $N_2O$ Band $\nu_1$ at $7.78 \mu$ (solar) compared with laboratory spectrum	<i>Astrophys. J.</i> 93, 509 (1941)	Atmospheric $N_2O$ identified
Adel	1941	Arizona	Grating Infrared Solar Spectrum Map $14 \mu$ to $7 \mu$	<i>Astrophys. J.</i> 94, 451 (1941); <i>Phys. Rev.</i> 59, 944 (1941)	Rotational lines of $\nu_1$ of $N_2O$ included. Abundance $N_2O$ 3 mm
Kriegel	1944	Oklahoma	Presence of $N_2O$ in Soil Air	<i>Geophys.</i> 9, 447 (1944)	Plausible source $N_2O$ in Soil Air terrier decomposition of vegetation
Adel	1946	Arizona	Evaluation of work of Kriegel	<i>Astron. J.</i> 52, 40 (1946); <i>Science</i> 103, 280 (1946)	Suggestion that Soil Air source of upper atmospheric $N_2O$
Migeotte	1948	Ohio State University	Telluric Bands of $N_2O$ at $3.9 \mu$ , $4.5 \mu$ and $8.6 \mu$	<i>Astron. J.</i> 54, 45 (1948)	Confirmed work of Adel and Sutherland
Shaw, Sutherland and Wormell	1948	Cambridge University, England	Bands of $N_2O$ at $3.90 \mu$ , $4.06 \mu$ and $4.5 \mu$	<i>Phys. Rev.</i> 74, 978 (1948)	Confirmed identification of $N_2O$ Unable to establish $7.8 \mu$ and $8.6 \mu$ bands
McMath and Goldberg	1949	Michigan	Bands of $N_2O$ at $2.13 \mu$ , $2.26 \mu$ and $2.97 \mu$ found	<i>Proc. Am. Philos. Soc.</i> 93, 363 (1949); <i>Astron. J.</i> 54, 214 (1949)	Abundance of $N_2O$ 4 mm $5 \times 10^{-4}$ percent by volume
Mohler and Pierce	1949	Michigan	Infrared solar spectrum $2.9 \mu$ to $3.6 \mu$ investigated	<i>Pub. Astron. Soc. Pacific</i> 61, 221 (1949)	Numerous lines of $N_2O$ near $3.0 \mu$ band
Adel	1950	Arizona	Temperature of atmospheric $N_2O$ layer	<i>Astron. J.</i> 55, 69 (1950); <i>Centen. Proc. Roy. Meteorol. Soc.</i> (1950)	Effective radiation temperature $0^\circ$ to $10^\circ C$ . $N_2O$ largely present in Troposphere
Benesch, Strong and Benedict	1950	Johns Hopkins University	Band of $N_2O$ at $2564 \text{ cm}^{-1}$ and $2461.5 \text{ cm}^{-1}$	<i>Prog. Report ONR Contract N5or 1-166</i> , August 1, 1950	The $2 \mu$ band of $N_2O$ at $2564 \text{ cm}^{-1}$ clearly resolved
Migeotte	1950	Ohio State University	Fine structure $N_2O$ bands	<i>Astrophys. J.</i> 112, 136 (1950)	Spectral regions $8.56 \mu$ to $8.84 \mu$ $4.46 \mu$ to $4.59 \mu$ studied
Shaw, Oxholm and Chapman	1950	Ohio State University	Fine structure $N_2O$ band near $4.06 \mu$	<i>Phys. Rev.</i> 78, 497 (1950)	Some 70 rotation lines in $4.06 \mu$ band observed
Slobod and Krogh	1950	Texas	Analysis of Surface Air	<i>J. Am. Chem. Soc.</i> 72, 1175 (1950)	Abundance of $N_2O$ in ground air same order of magnitude as from solar spectra absorption data

Table V. The Discovery, Identification and Vertical Distribution of Atmospheric Nitrous Oxide (Continued)

Investigator	Date	Place	Discovery	Reference	Remarks
Adel	1951	Arizona	Summary of lines of evidence of origin atmospheric $N_2O$	<i>Science</i> 113, 624 (1951)	Origin of $N_2O$ . Soil air an important source
Gebbie, Harding et al.	1951	England	Atmospheric transmission in the 1 to 14 $\mu$ region	<i>Proc. Roy. Soc. (London)</i> A 206, 87 (1951)	$N_2O$ present in atmosphere at sea level. Elevation over paths up to 4 km
Adel	1952	Arizona	Second fundamental of $N_2O$ $\nu_1$ at 17.0 $\mu$ discovered	<i>Phys. Rev.</i> 88, 128 (1952)	$\nu_1$ at 7.8 $\mu$ , $\nu_2$ at 17.0 $\mu$ and $\nu_3$ at 4.5 $\mu$ have now all been identified
Bates, and Bates and Witherspoon	1952	England	Photochemistry of $N_2O$ from homogeneous gas reactions probable in upper atmosphere	<i>Ann. Geophys.</i> 8, 194 (1952); <i>Mon. Not. Roy. Astron. Soc.</i> 112, 101 (1952)	$N_2O$ at 70 km and 30 km considered
Migotte and Neven	1952	Jungfraujoch Observatory, Switzerland	Solar spectrum from 15 $\mu$ to 24 $\mu$ studied	<i>Astrophys. J.</i> 115, 326 (1952); <i>Mem. Soc. Roy. Sci. Liege</i> 12, 165 (1952)	Observation of atmospheric $N_2O$ in Switzerland
Shaw, Oxholm and Claassen	1952	Ohio State University	Reinvestigation of spectral region 7 to 13 $\mu$	<i>Astrophys. J.</i> 116, 551 (1952)	Many more lines in the 2 $\nu$ band of $N_2O$ observed
Goldberg and Muller	1953	Michigan	Vertical Distribution of $N_2O$ studied	<i>J. Opt. Soc. Am.</i> 43, 1033 (1953)	$N_2O$ uniformly mixed with the major constituents of atmosphere. Concentration contained in lower layers. Not higher than 15 km
Goody and Walshaw	1953	Cambridge University, England	Origin of atmospheric $N_2O$	<i>Quart. J. Roy. Meteorol. Soc.</i> 79, 496 (1953)	Bacterial reactions in the soil the primary source of atmospheric $N_2O$ . Homogeneous gas reactions in upper atmosphere of secondary importance

Table VI. Elevation of Observatories Obtaining Data on  $N_2O$ 

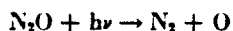
Station	Elevation in meters
McMath-Hulbert Observatory, Lake Angelus, Michigan	296
Mount Wilson Observatory, California	1742
Lowell Observatory, Flagstaff, Arizona	2210
McMillin Observatory, Columbus, Ohio	233
University Observatory, Cambridge, England	28
Sacramento Peak, New Mexico	2760
Jungfraujoch, Switzerland, International Scientific Station	3580

(a) *From soil air.* In studying the analyses of certain hydrocarbons at the Laboratories of the Carter Oil Company, Tulsa, Oklahoma, Kriegel (1944) identified nitrous oxide as a constituent in these gases. He gave reasons for believing that nitrous oxide exists in soil air, and suggested as a plausible source of nitrous oxide in soil air the slow decomposition of commercial fertilizers, especially in farming regions. Studies of decomposition of vegetation under aerobic conditions show that nitrous oxide forms a large portion of the condensed gas fraction in soil air.

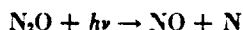
Basing his theory upon the discovery of Kriegel, Adel (1946) suggested that soil air might be one source, and perhaps the principal one, of the atmospheric nitrous oxide layer in the atmosphere. Later Adel (1951) summarized the several lines of evidence to support this early hypothesis of the origin of atmospheric nitrous oxide: (1) A British Admiralty group found from infrared atmospheric transmission that large concentrations of nitrous oxide were present in paths parallel and close to the surface of the land and sea; (2) Solar spectra recorded aboard high-flying aircraft revealed a greatly diminished absorption of nitrous oxide in the  $7.8\mu$  region with height, and (3) Slobod and Krogh (1950) from a mass spectroscopic analysis of ground samples of air found the concentration of nitrous oxide to be about  $5 \times 10^{-5}$  percent by volume, that is, of the same order of magnitude as that deduced from infrared absorption methods. The following cycle was proposed by Adel:

Nitrous oxide appears in the soil as a decomposition product of the fixed nitrogen compounds. It diffuses into the atmosphere. In the upper atmosphere nitrous oxide is decomposed photochemically by  $\lambda < 2000 \text{ \AA}$  into  $\text{N}_2$ ,  $\text{O}_2$  and  $\text{NO}$ . At these high atmospheric levels  $\text{NO}$  is also decomposed photochemically into nitrogen and oxygen by  $\lambda < 2000 \text{ \AA}$ . The nitrous oxide presumably accumulates above the earth's surface until the rates of accumulation and decomposition are equal.

(b) *From homogeneous gas reactions in the upper atmosphere.* Bates (1952), and Bates and Witherspoon (1952) employing absorption cross sections derived from several laboratory investigations of different groups of investigators have calculated the rate of photodissociation by

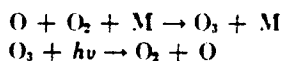


which begins at about  $\lambda 3700 \text{ \AA}$ , and the reaction

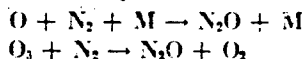


which begins at about  $\lambda 2400 \text{ \AA}$ . Two levels of nitrous oxide were considered, ground level and the 70-km level. It was assumed that all the nitrous oxide is contained in a 10-km layer at one or the other of these levels. The calculations show that if the layer were at ground level the number of  $\text{N}_2\text{O}$  molecules destroyed by photodissociation would be some  $5 \times 10^4 \text{ cm}^2 \text{ sec}$ . At the 70-km level the number would be some  $3 \times 10^7 \text{ cm}^2 \text{ sec}$ .

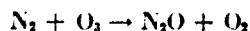
These are large destruction rates and in order to account for them Bates and Witherspoon considered that the only plausible parent particles are the  $\text{O}$  atoms and  $\text{O}_3$  molecules in the *lower atmosphere* by which equilibrium is preserved by the following reactions.



The formation of nitrous oxide might result from the following reactions which are considered the most favorable and sufficient to meet the nitrous oxide requirement.

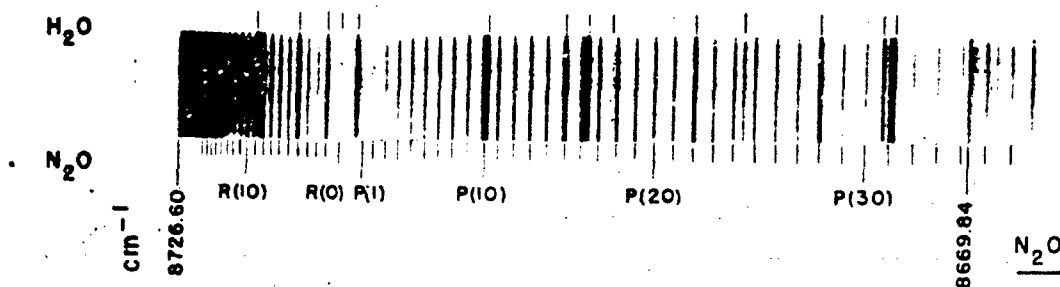


More recently the question as to the origin of atmospheric nitrous oxide has been studied by Goody and Walshaw (1953) of the Cavendish Laboratory, Cambridge, England. From new observational data they were able to make an estimate of the rate of the reaction,



which was considered by Bates and Witherspoon as being the most promising of the homogeneous gas reactions for the production of atmospheric nitrous oxide.

Goody and Walshaw studied the rate of the above reaction by mixing nitrogen and ozone in an absorption tube, measuring the ozone decay from the absorption in the Chappuis bands (6020, 5872, and 5750 Å), and the nitrous oxide formed from the intensity in the  $7.8 \mu$  band. The rate coefficient was deduced to be less than, or equal to,  $5 \times 10^{-28} \text{ cm}^3 \text{ sec}^{-1}$  at  $19^\circ\text{C}$  as compared to  $5 \times 10^{-27} \text{ cm}^3 \text{ sec}^{-1}$  obtained by Bates and Witherspoon. Wall reaction effects and other factors were considered. The evidence obtained by Goody and Walshaw indicated that the homogeneous gas reaction mechanism proposed by Bates and Witherspoon is too slow by a factor of 40 to account for the observed concentration of nitrous oxide in the atmosphere.



Courtesy of Gerhard Herzberg, National Research Council, Ottawa, Canada.

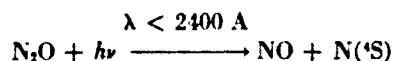
Fig. 2. A spectrogram of the  $4.5 \mu$  band of  $\text{N}_2\text{O}$  at  $1.15 \mu$ . This band in the photographic infrared has the P and R branches only. The spectrum of  $\text{N}_2\text{O}$  was studied below  $1.2 \mu$  with long absorbing paths up to 4500 m atmos. In this spectral region the bands of  $\text{N}_2\text{O}$  are overlapped by the great  $\text{H}_2\text{O}$  band near  $1.15 \mu$ . The positions of the  $\text{N}_2\text{O}$  lines are indicated below the spectrogram, while the  $\text{H}_2\text{O}$  lines are shown above it.

As a result of these observational data the emphasis has been reversed and is favorable toward bacterial reactions in the soil to be probably the principal source of atmospheric nitrous oxide. The rate of production is considered sufficient to compensate the photochemical decomposition. The homogeneous gas reaction theory according to this more recent quantitative study is of less and secondary importance. One might conclude that there are these two processes in operation to supply nitrous oxide to the earth's atmosphere. Additional data are probably needed to decide definitely which might be considered to be the more important.

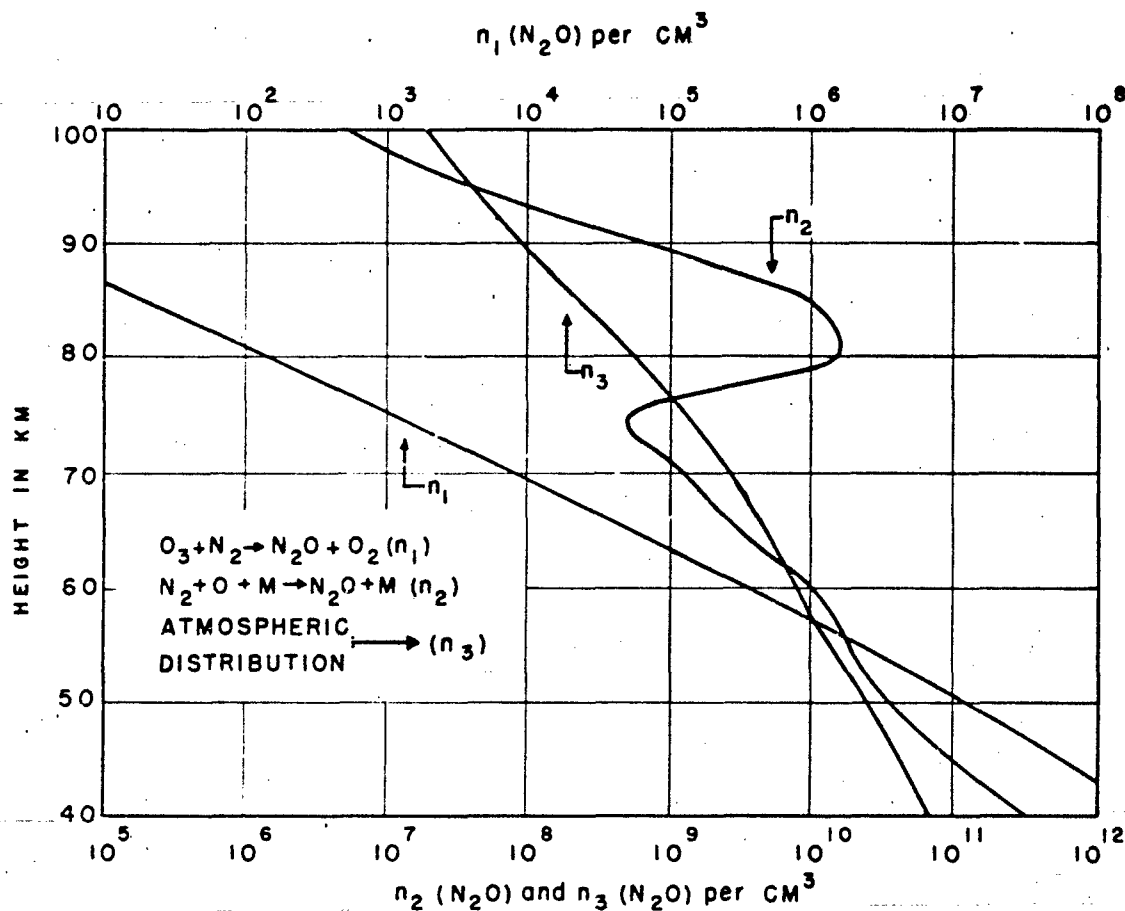
#### 1.4.3 Vertical distribution of $\text{N}_2\text{O}$ in the atmosphere

Various estimates have been made about the vertical distribution of nitrous oxide in the earth's atmosphere. Some favor the hypothesis that it is concentrated in the lower layers of the atmosphere, in the

troposphere and lower stratosphere, and is uniformly mixed falling off in concentration with height similar to the other permanent atmospheric constituents. Others believe that the nitrous oxide is present in the upper atmosphere in sufficient amount to account for the formation of nitric oxide

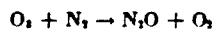


at altitudes of 80 to 90 km. The following table summarizes statements in the literature about the vertical distribution, while the following figure by A. P. Mitra gives the vertical distribution in the upper atmosphere from homogeneous gas reactions believed to occur at these higher altitudes.

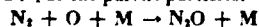


From A. P. Mitra. Ionospheric Research, Scientific Report No. 46, The Pennsylvania State College.

Fig. 3. The vertical distribution of  $\text{N}_2\text{O}$  in the upper atmosphere. The distribution ( $n_1$ ) was calculated on the assumption that the parent particles in  $\text{N}_2\text{O}$  formation are from  $\text{O}_3$  and  $\text{N}_2$



The distribution ( $n_2$ ) considers atomic oxygen and  $\text{N}_2$  as the parent particles.



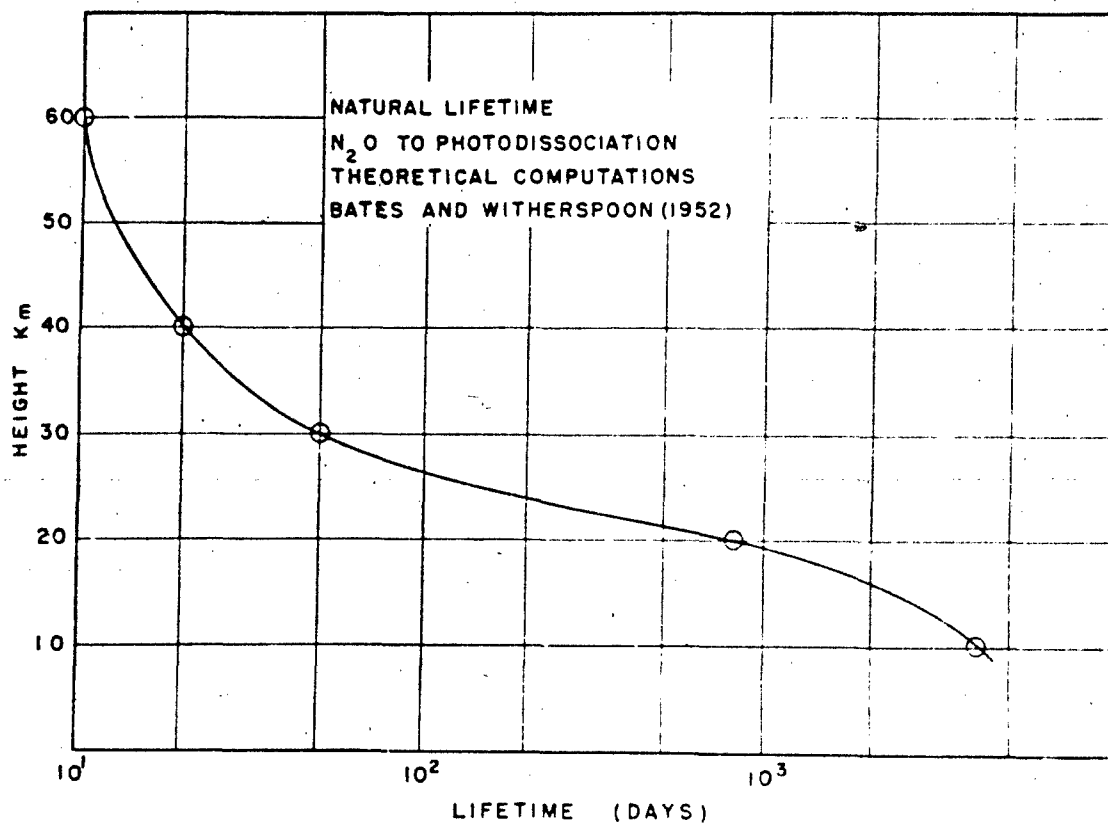
The infrared absorption bands of such minor gaseous constituents of the atmosphere, such as  $\text{H}_2\text{O}$ -vapor,  $\text{CO}_2$ ,  $\text{O}_3$ ,  $\text{N}_2\text{O}$ , etc., have been most widely employed to detect and measure their distribution. Line intensities, the nature of line-broadening mechanisms, the consequent line shape, the line widths and the effect of

temperature and pressure upon them are useful to permit quantitative interpretation of nitrous oxide in the solar spectrum recorded at different levels in the atmosphere.

The papers by Adel (1950), Goldberg and Müller (1953), and Goody and Walshaw (1953) probably give the latest quantitative data upon the vertical distribution of  $N_2O$ . The method used by Adel was the measurement of the effective radiation temperature for the  $N_2O$  layer in the earth's atmosphere from measurements of its emissivity and radiation intensity at  $7.8 \mu$ . The method is a general one and applicable to other atmospheric gases, such as ozone.

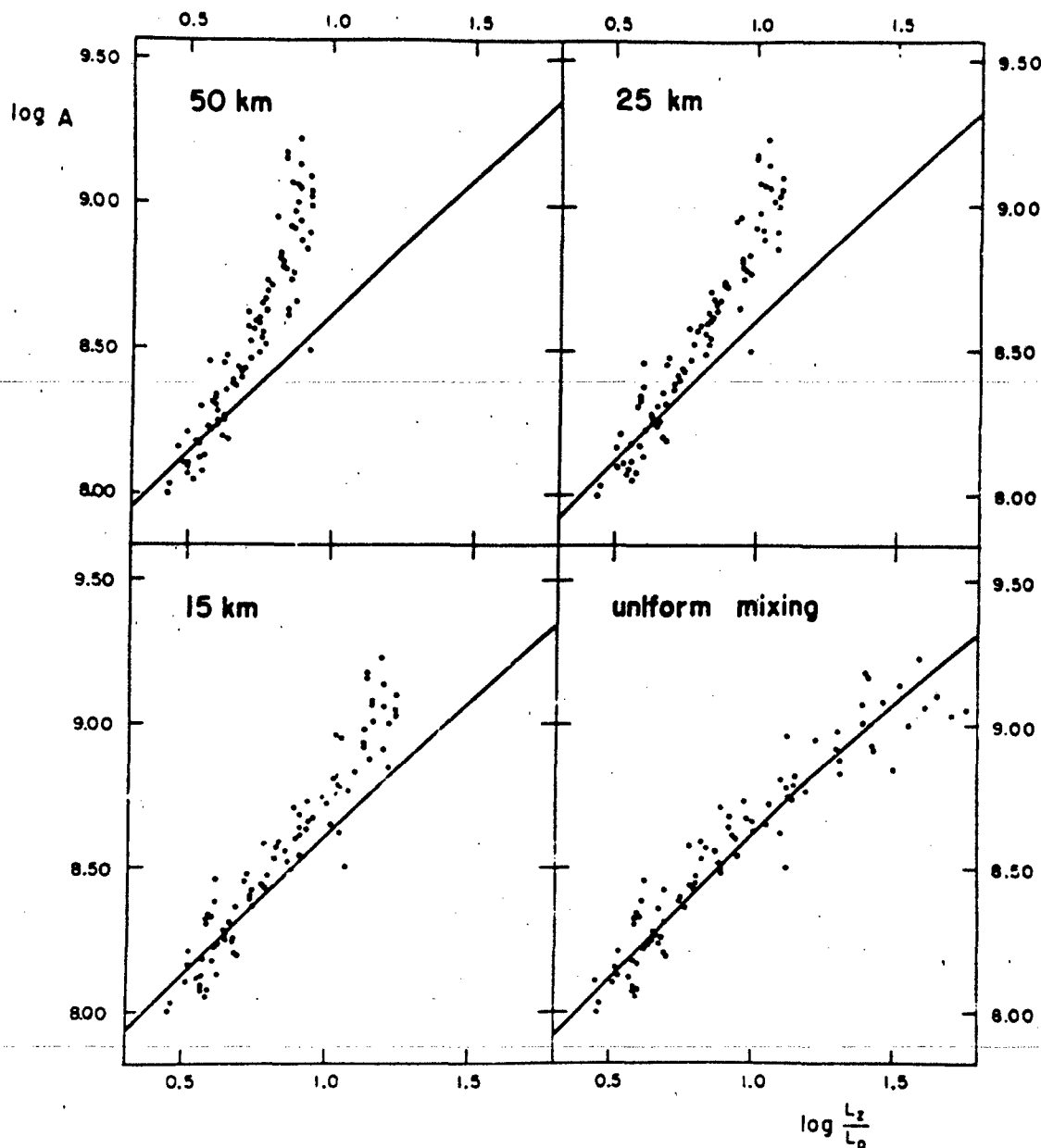
Assuming that the nitrous oxide is present in an isothermal layer which is a largely unknown factor for  $N_2O$ , Adel found effective radiation temperatures between  $0^\circ$  and  $10^\circ C$ . This temperature range for  $N_2O$  coupled with the well developed distribution of rotational intensities in the atmospheric absorption bands indicated that nitrous oxide is concentrated mostly in the troposphere.

Goldberg and Müller (1953) have determined the vertical distribution of nitrous oxide in the earth's atmosphere by the *low-sun method*. The principle involved in this method is that in a curved atmosphere, the amount of absorbing gas traversed by a ray of sunlight from directions near the horizon depends upon the vertical distribution. The relative amounts of absorbing gas traversed by light rays coming from different zenith angles of the sun were calculated from the Link and Sekera tables (*Publ. Nat. Obs.*, Prague, 14 (1940)). The values in these tables are based on the observed density distribution in the atmosphere and take into



From Goody and Walshaw, and Bates and Witherspoon.

Fig. 4. Natural lifetime of a molecule of  $N_2O$  to photodissociation at different altitudes from theoretical considerations of Bates and Witherspoon (1952).



Courtesy of Leo Goldberg and Edith A. Muller, McMath-Hulbert Observatory, University of Michigan  
 Fig. 5. Empirical curves of growth for  $N_2O$  assuming that  $N_2O$  is concentrated in a layer of uniform density 5-km thick at altitudes of (a) 50, (b) 25, and (c) 15 km, and (d) that  $N_2O$  has the same vertical distribution as the main body of the atmosphere.

The relation between the total absorption of a line and its integrated absorption coefficient defines the so-called curve of growth. The ordinate ( $\log A$ ) is the logarithm of the total absorption in  $\text{sec}^{-1}$ . The abscissa is the  $\log L_2/L_0$  (path length in air masses).

The solid line is the lower, linear end of a theoretical curve of growth for pure collisional broadening with  $\gamma/2\pi = 2.0 \times 10^4 \text{ sec}^{-1}$ . It may be observed that for  $L_2/L_0 > 10$  ( $\log L_2/L_0 > 1$ ) uniform mixing is the only graph in accord with the observations, while when the number of air masses is less than four all four assumptions of vertical distribution are in accord with the observations.

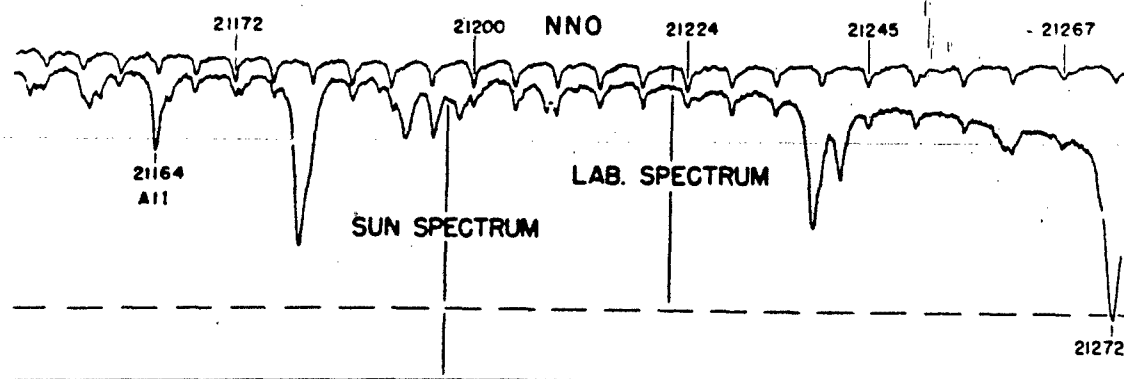


Table VII. Vertical Distribution of Atmospheric Nitrous Oxide

Author	Date	Place	Height	Reference
Adel	1950	Arizona	Largely present in the troposphere	<i>Astron. J.</i> 55, 69 (1950); <i>Centen. Proc. Roy. Meteorol. Soc. (London)</i> , pp. 5-8 (1950)
Bates and Nicolet	1950	(Theoretical)	Lack of data on vertical distribution. Probably confined to troposphere	<i>J. Geophys. Research</i> 55, 306 (1950)
Slobod and Krogh	1950	Texas and Wyoming	Ground air not merely a thin layer, distributed throughout the atmosphere	<i>J. Am. Chem. Soc.</i> 72, 1175 (1950)
Wormell	1950	England	Occurs in lowest layers of the atmosphere	<i>Centen. Proc. Roy. Meteorol. Soc. (London)</i> , p. 30 (1950)
Gebbie and Others	1951	England	Present at sea level and up to 4 km	<i>Proc. Roy. Soc. (London)</i> A206, 87 (1951)
Bates	1952	(Theoretical)	Prevalent in the troposphere	<i>Ann. Geophys.</i> 8, 194 (1952)
Goldberg and Müller	1953	Michigan	Lower levels of the atmosphere, not higher than 15 km	<i>J. Opt. Soc. Am.</i> 43, 1033 (1953)
Goody and Walshaw	1953	England	Uniformly mixed up to 10 km and probably 40 km	<i>Quart. J. Roy. Meteorol. Soc.</i> 79, 496 (1953)

account the refraction. Densities up to 20 km were taken from "Physics in the Atmosphere" by Humphreys, McGraw-Hill Book Company, Inc., New York (1940).

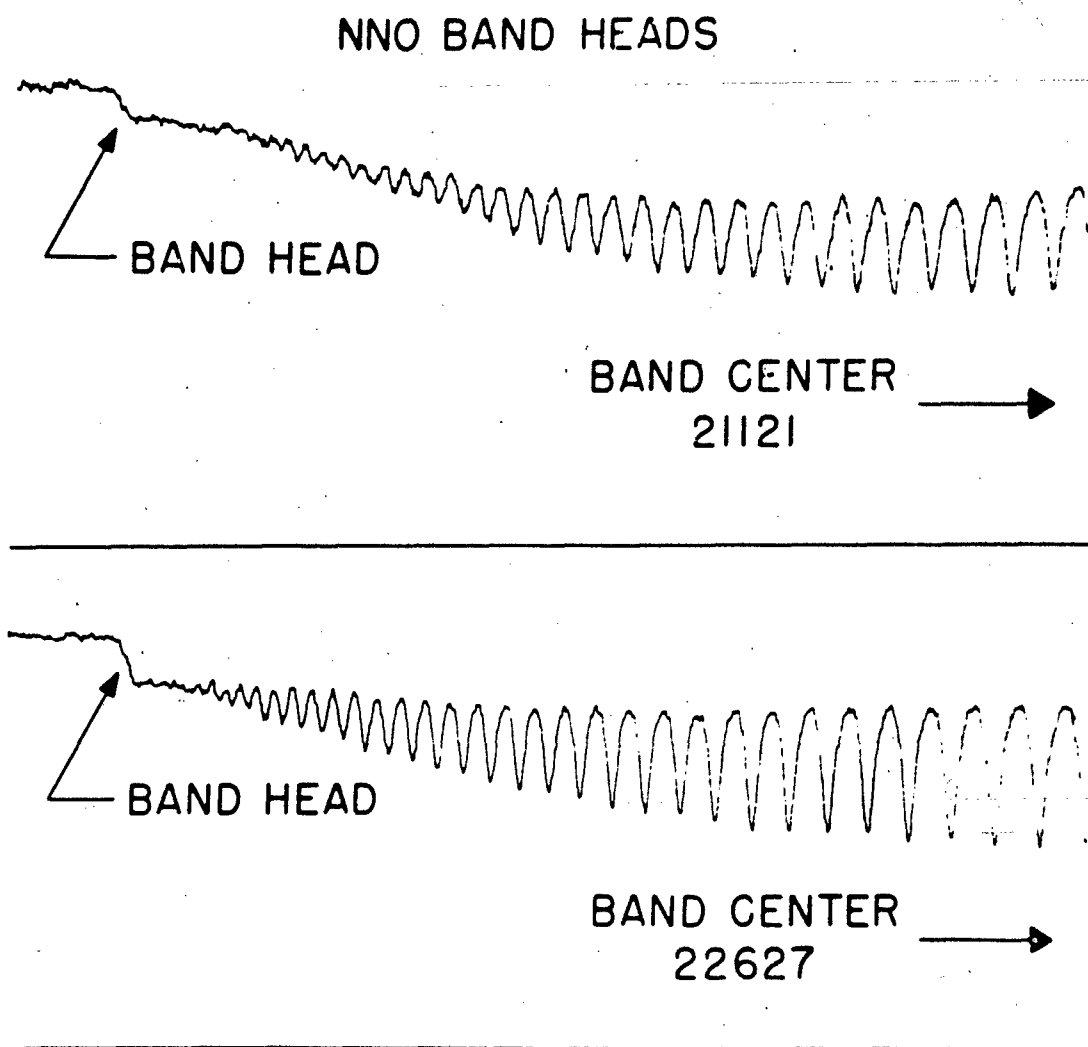
The quantity  $L_z/L_0$ , the path length in the air masses, was calculated, where  $L_z$  and  $L_0$  are the total amounts of absorbing gas in direction of the zenith angle,  $z$ , and through the zenith. It was assumed that the vertical distribution of nitrous oxide is concentrated in a layer of uniform density 5-km thick at altitudes 15, 25, and 50 km, and that the  $N_2O$  has the same vertical distribution as the main body of the atmosphere. Empirical curves of growth for  $N_2O$  on the above assumptions as to vertical distribution show that the line intensities for  $N_2O$  observed at low solar altitudes seem definitely to rule out the concentration of  $N_2O$  in layers at altitudes of 15 km or higher in the earth's atmosphere, and resides mostly in the lower levels of the atmosphere.



Courtesy of Dr. Robert R. McMath and Dr. Leo Goldberg, McMath-Hulbert Observatory, University of Michigan.  
Fig. 6. The band of  $N_2O$  at  $2.13 \mu$ . From the comparison of the intensities of the bands in the earth's atmosphere (telluric spectrum) and a known amount of  $N_2O$  in a laboratory spectrum, the equivalent abundance of  $N_2O$  in the earth's atmosphere was determined.

#### 1.4.4 Abundance of atmospheric nitrous oxide

The various values that have been obtained for the abundance of nitrous oxide in the earth's atmosphere are listed in the following table. These values were obtained in most cases from infrared absorption methods. For example, the abundance of atmospheric  $\text{N}_2\text{O}$  was determined by McMath and Goldberg (1949) by comparing the intensities of the lines of the  $2.13 \mu$  band in the solar spectrum with that produced by a known amount of  $\text{N}_2\text{O}$  from laboratory experiments. The telluric absorption was found to be equivalent to that which would be produced by 4 mm of  $\text{N}_2\text{O}$  at NTP. While the values obtained by various investigators vary from 3-10 atmo-mm (NTP), it might be concluded that they are remarkably constant considering the differences in elevation of the observing stations.



Courtesy of Dr. Robert R. McMath and Dr. Leo Goldberg, McMath-Hulbert Observatory, University of Michigan.  
 Fig. 7. Laboratory infrared spectrum of  $\text{N}_2\text{O}$  in the  $2 \mu$  spectral region. The two bands located at  $2.13 \mu$  and  $2.26 \mu$  are absorption bands which may be observed in the solar spectrum.

Table VIII. Abundance of Nitrous Oxide in the Atmosphere

Author	Date	Place	Abundance atmo-mm NTP	Reference
Adel	1939	Arizona	Several mm	<i>Astrophys. J.</i> 90, 627 (1939)
Adel	1941	Arizona	3	<i>Phys. Rev.</i> 59, 944 (1941)
Sutherland and Callendar	1942	England	8	<i>Reports Prog. Phys.</i> 9, 18 (1942-43)
Shaw, Sutherland, and Wormell	1948	England	10	<i>Phys. Rev.</i> 74, 978 (1948)
McMath	1949	Michigan	4	<i>Astron. J.</i> 54, 214 (1949)
McMath and Goldberg	1949	Michigan	4	<i>Proc. Am. Philos. Soc.</i> 93, 363 (1949)
Adel	1950	Arizona	5	<i>Centen. Proc. Roy. Meteorol. Soc.</i> (London), pp. 5-8 (1950)
Goldberg	1950	Michigan	4	<i>Reports Prog. Phys.</i> 13, 24 (1950)
McMath and Others	1950	Michigan	4	<i>Phys. Rev.</i> 78, 65 (1950)
Slobod and Krogh	1950	Texas and Wyoming	$5 \times 10^{-1}$ percent by volume	<i>J. Am. Chem. Soc.</i> 72, 1175 (1950)

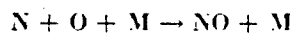
## 1.5 NITRIC OXIDE AND OTHER OXIDES OF NITROGEN IN THE ATMOSPHERE

## 1.5.1 Nitric oxide (NO)

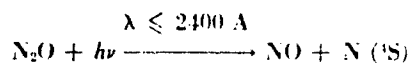
The definite identification of the presence of nitric oxide as a permanent constituent of the earth's atmosphere has not up to the present time (1955) been established by direct observation. From the analysis of the solar spectra from Rocket flights on 10 October 1946 and 7 March 1947, Durand, Oberly and Tousey (1949) of NRL found the structure between  $\lambda\lambda$  2200 Å and 2300 Å could be caused by atmospheric bands of NO, since the spectrum could not be interpreted in terms of known atomic lines. Later (1953) Johnson and other workers at NRL with the aid of more intense exposures have studied the existence of atmospheric nitric oxide further. From a densitometer tracing of the solar spectrum and the positions of the nitric oxide band heads it appeared that nitric oxide is not present in sufficient quantity in either the earth's or the sun's atmosphere to cause significant absorption in this spectral region.

Migeotte and Neven (1952) also were unable from infrared studies to find the presence of atmospheric nitric oxide. They concluded that no more than 0.02 cm NTP of nitric oxide could be present in the earth's atmosphere. This value sets a rather upper limit for the abundance of this oxide of nitrogen in the atmosphere.

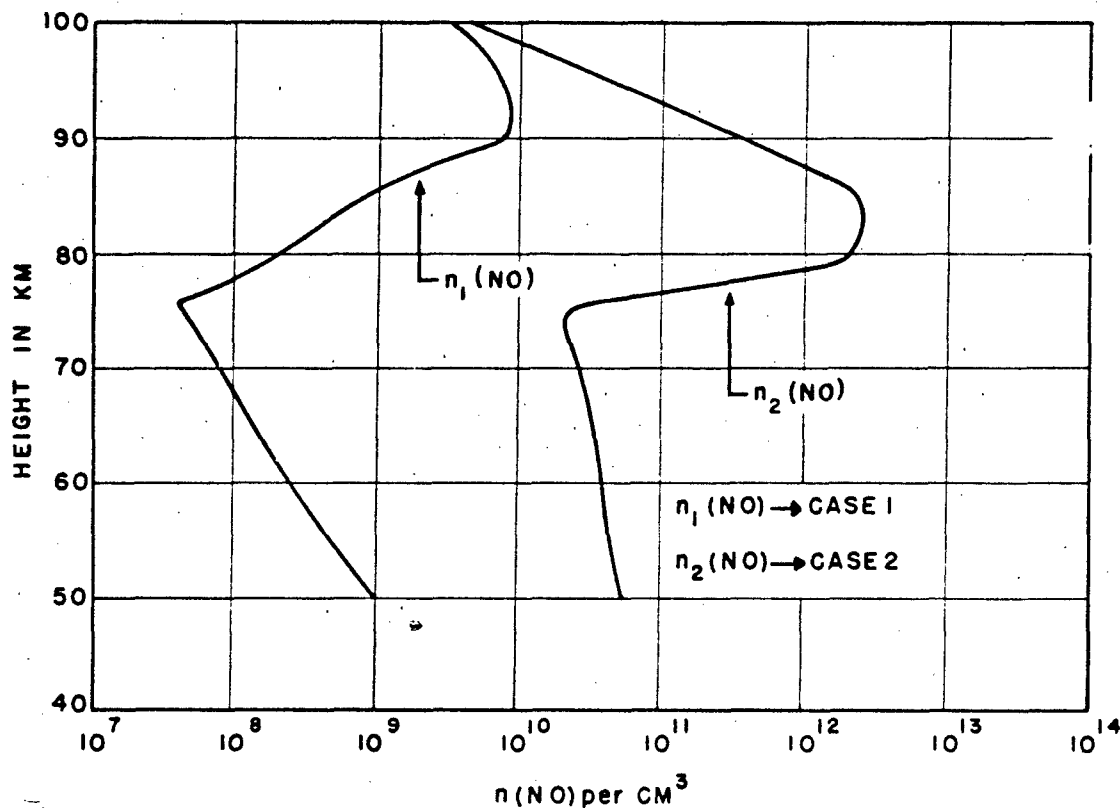
From theoretical considerations Nicolet (1945) deduced that nitric oxide should be an important constituent in the higher altitudes of the atmosphere below the transition region where molecular oxygen is dissociated into atomic oxygen. The following two processes were considered possible for the production of nitric oxide in the upper atmosphere. In a region where there are sufficient numbers of atomic nitrogen and oxygen atoms the three body reaction may occur.



A second possible mechanism for nitric oxide production is the photodissociation of nitrous oxide into atomic nitrogen and nitric oxide.

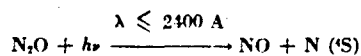


In the table on page 18 the various statements in the literature with reference to the presence of nitric oxide in the atmosphere are summarized. While references to the theoretical possibility of atmospheric nitric oxide are abundant, and there is much supporting evidence in photochemical and photoionization processes for its existence, and its importance in excitation phenomena, the direct discovery from observational data still remains a scientific goal to be achieved.

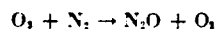


From A. P. Mitra. Ionospheric Research, Scientific Report No. 46, The Pennsylvania State College.

Fig. 8. The vertical distribution of NO in the upper atmosphere. The distribution  $n_1(\text{NO})$  considers the formation of NO from the dissociation of  $\text{N}_2\text{O}$



if  $\text{N}_2\text{O}$  is formed from



The distribution  $n_2(\text{NO})$  considers the NO to come from  $\text{N}_2\text{O}$  formed by the reaction

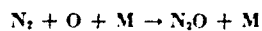
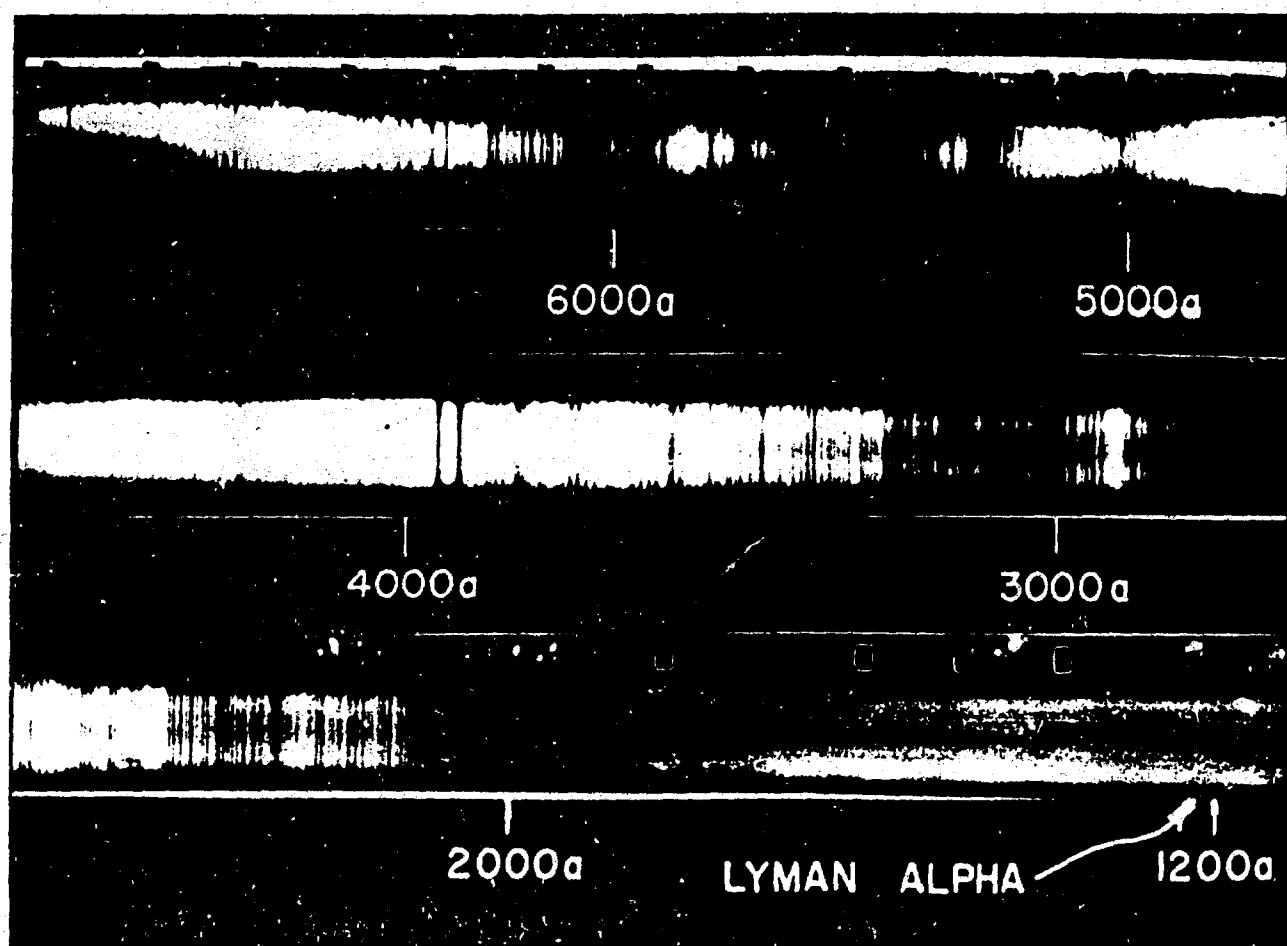


Table IX. The Presence of Nitric Oxide in the Atmosphere

Author	Date	Statement	Reference
Kaplan	1939	NO bands present in light of night sky but not observed due to ozone absorption	<i>Nature</i> 144, 152 (1939)
Elvey, Swings and Linke	1941	Presence of the $\beta$ -bands of NO in the night sky not ascertained, nor has it been excluded	<i>Astrophys. J.</i> 93, 337 (1941)
Elvey	1942	Both the $\beta$ -bands and the $\gamma$ -bands may be present in the spectrum of the non-polar aurora	<i>Rev. Mod. Phys.</i> 14, 140 (1942)
Price	1942	NO may be present as an important atmospheric constituent due to photodissociation of $N_2O$ and reaction of $N_2O$ with atomic oxygen and a third body	<i>Reports Prog. Phys.</i> 9, 10 (1942-43)
Nicolet	1945	NO an important constituent in the upper atmosphere	<i>Inst. Roy. Meteorol., Belgium Memoires</i> 19, 124 (1945)
Wooley	1946	NO may be a source of electrons in the F <sub>1</sub> layer	<i>Proc. Roy. Soc. (London)</i> A 187, 414 (1946)
Bates and Massey	1947	NO may be found in upper atmosphere by collision of atomic nitrogen with atomic oxygen	<i>Proc. Roy. Soc. (London)</i> A 192, 1 (1947)
Nicolet	1948	NO and O <sub>2</sub> characterize the atmospheric range of the E layer, and aurora	<i>Phys. Soc. (London)</i> "Emission Spectra etc." (1948)
Durand, Oberly, and Tousey	1949	The NO band at $\lambda$ 2264 Å in Rocket ultraviolet solar spectra could be interpreted as atmospheric bands of NO	<i>Astrophys. J.</i> 109, 1-16 (1949)
Nicolet	1949	Reaction of $N + O \rightarrow NO$ possible in the upper atmosphere	<i>J. Geophys. Research</i> 54, 373 (1949)
Bates and Nicolet	1950	Although amount of NO in the atmosphere unknown, it is probably present due to photodissociation of $N_2O$	<i>J. Geophys. Research</i> 55, 306 (1950)
Bates and Seaton	1950	Not unlikely that NO is an important constituent of the upper atmosphere	<i>Proc. Phys. Soc. (London)</i> 63 B, 129 (1950)
Bates	1951	In the absence of evidence to the contrary it seems best to assume that NO is a very minor constituent at all levels	<i>Proc. Phys. Soc. (London)</i> 64 B, 805 (1951)
Mitra, A. P.	1951	A reference to Nicolet who considered ionization of NO at $\lambda$ 1300 Å a process in the D layer formation	<i>J. Geophys. Research</i> 56, 373 (1951)
Bates	1952	If atomic nitrogen and NO are constituents of the upper atmosphere, then NO <sub>2</sub> should also exist	<i>Ann. Geophys.</i> 8, 194 (1952)
Nicolet and Mange	1952	The NO molecule is an important constituent in the D region	Scientific Report No. 35, Penn State (1952)
Migeotte and Neven	1952	Unable to find atmospheric NO from infrared studies. No more than 0.02 cm NTP present in the earth's atmosphere	<i>Mém. Soc. Roy. Sci., Liège</i> 12, 165 (1952)
Vegard, Kvifte and Tonsberg	1952	Observed the $\beta$ -band of NO in the spectrum of the auroral luminescence at $\lambda\lambda$ 5256, 4913, 4030, 3961, and 3880 Å	<i>Geofys. Publ.</i> 18, No. 3 (1951); <i>ibid.</i> 18, No. 8 (1952)
Byram and Others	1953	Lyman-alpha observed at 74 km in solar spectrum from Rockets. Absorption of H $\gamma$ radiation may produce D-layer ionization	<i>Phys. Rev.</i> 91, 1278 (1953)
Johnson and Others	1953	Reference made to previous report by Durand and others of atmospheric NO. Double bands of NO at 2265 Å and 2150 Å studied thoroughly. No evidence for presence of NO in either the terrestrial or solar atmosphere	Gassiot Meeting, August (1953)

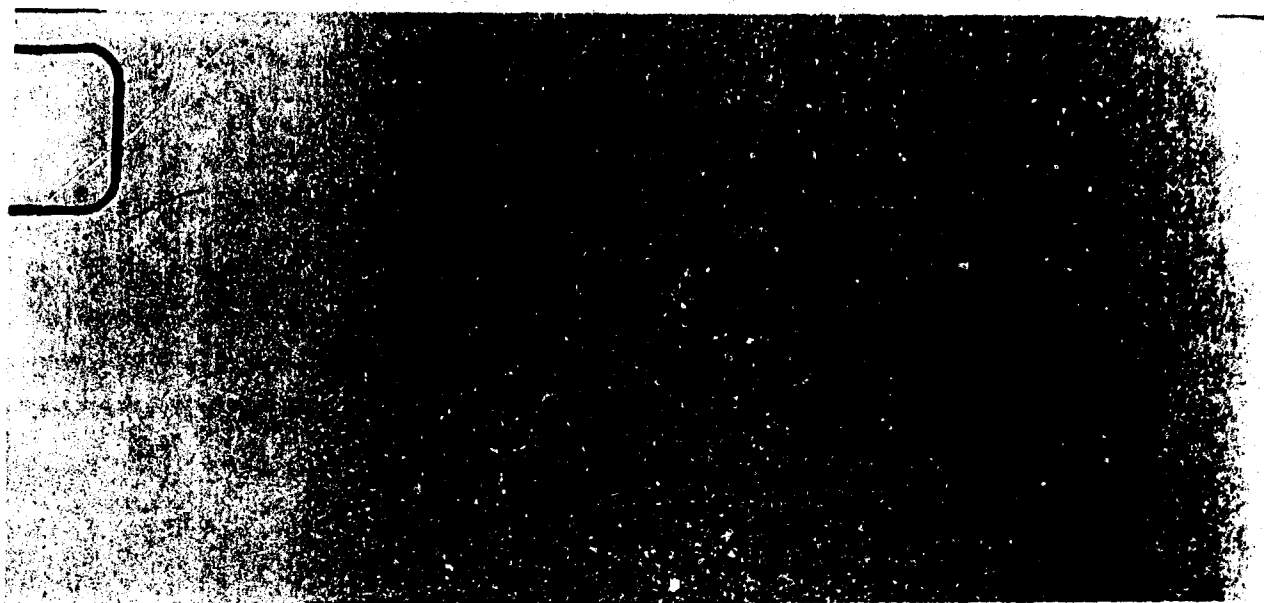
Table IX. The Presence of Nitric Oxide in the Atmosphere (Continued)

Author	Date	Statement	Reference
Mitra, A. P.	1953	The broad band between 2200 and 2300 Å might come from NO existing in sun's atmosphere	Scientific Report No. 46, Penn State (1953)
Nicolet	1953	From theoretical considerations NO is possible quite abundant below region where O <sub>2</sub> is dissociated into O	Scientific Report No. 52, Penn State (1953)
Watanabe and Others	1953	Absorption cross sections of O <sub>2</sub> and NO and photoionization of NO determined. Supports theory of NO ionization mechanisms for the formation of the D layer	<i>Phys. Rev.</i> 90, 155 (1953); <i>ibid.</i> 91, 436 (1953); <i>ibid.</i> 91, 1155 (1953)



Courtesy of Dr. William A. Rense, University of Colorado, Boulder, Colorado.

Fig. 9. A Spectrogram showing the Lyman-alpha line. The spectrogram was obtained by photographing the Sun's spectrum during a rocket firing 12 December 1952 with a grazing-incident spectrograph during a 28-second exposure by a biaxial sun-follower in an Aerobee rocket. This discovery together with the detection of solar radiation between 1180 Å and 1300 Å with the aid of photon counters flown in rockets and reported by Byram, Chubb, Friedman, and Lichtman (1953) who detected Lyman-alpha radiation at a depth of about 74 km; and the recent investigations by Watanabe, Marmo and Inn (1953) on the absorption cross section and photoionization of nitric oxide (NO) at the Lyman-alpha wavelength (1216 Å) lend support to the theory that the photoionization of NO is a plausible mechanism for the formation of the D layer.



Courtesy of Dr. William A. Rense, University of Colorado, Boulder, Colorado.

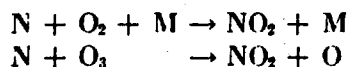
Fig. 10. Lyman-alpha line (1216 Å) greatly enlarged from first printing on the film of Fig. 9. Approximate magnification X 10.

#### 1.5.2 Nitrogen dioxide (NO<sub>2</sub>) in the upper atmosphere

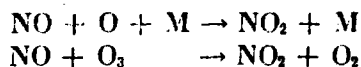
In discussing absorption spectra and absorption coefficients of atmospheric gases, Price (1942-43) considers nitrogen dioxide. He states that if much nitric oxide (NO) is present in the upper atmosphere some nitrogen dioxide might be formed during the night. The absorption of radiation of wavelengths from 6000 Å to 3700 Å and in the shorter wavelengths by nitrogen dioxide would limit the amount of nitrogen dioxide in the atmosphere during the day.

Bates (1952) also has studied the possibility for the existence of NO<sub>2</sub> in the upper atmosphere. If atomic nitrogen and nitric oxide are constituents of the upper atmosphere, nitrogen dioxide should also be present. Bates has suggested the following mechanisms to account for the formation of nitrogen dioxide in the upper atmosphere.

##### (a) Direct combination.



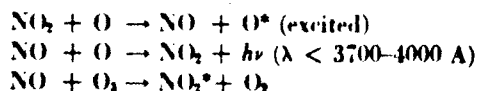
##### (b) Oxidation of nitric oxide.



It should be remarked that these reactions are merely speculative, as much requisite basic data are lacking to establish positive evidence of the occurrence of NO<sub>2</sub> in the upper atmosphere.

Nicolet (1953) has considered the photochemistry of nitrogen dioxide in the upper atmosphere along with (a) nitrous oxide and (b) nitric oxide which generally are regarded to be the most important of the oxides of nitrogen at high levels and in ionospheric phenomena. Nicolet states that nitrogen dioxide is not considered an important constituent in the mesosphere (I. U. C. G. nomenclature) during daylight, since the rate coefficient of dissociation is high. Nitrogen dioxide processes during the night have not been investigated, however several laboratory studies on radiative processes indicate that nitrogen dioxide may be an

important contributor to the continuous airglow spectrum. The following reactions were suggested by Nicolet which might be important mechanisms in the night airglow.



### 1.5.3. The role of nitrogen oxides (NO and NO<sub>2</sub>) in smog conditions

As early as 1923 Reynolds studied the formation of nitrogen dioxide and ozone during thunderstorms over London, England in order to answer questions as to what chemical changes, if any, are associated with atmospheric electrical discharges. Later in 1930 Reynolds noted that nitrogen dioxide was essentially a constituent of town air, there being about six times as much nitrogen dioxide in the air over the City of London as the amount measured at Upminster, a suburban district.

In view of the great interest of knowing the amounts of the oxides of nitrogen in the atmosphere, several quantitative methods have been developed for the determination of the oxides of nitrogen in air. A summary of various analytical methods is given in Table X. In general most of the methods are basically colorimetric procedures, and have sensitivities of the order of one part per million, or less, by volume.

Table X. Determination of Oxides of Nitrogen

Author	Method	Sensitivity	Reference
Francis and Parsons	Oxidation with H <sub>2</sub> O <sub>2</sub> Colorimetric Phenoldisulfonic acid	Less than 1 ppm	<i>Analyst</i> 50, 262 (1925)
Edgar and Paneth	NO <sub>2</sub> absorbed on silica gel at -120°C. Subsequent oxidation with H <sub>2</sub> O <sub>2</sub> colorimetric 2:4-xylene-1-ol	Less than 1 ppm	<i>J. Chem. Soc.</i> (1941) 519-527
Beyer	NO <sub>2</sub> (a) Titrimetric by reduction to NH <sub>3</sub> . (b) Photometrically by color with Hoesly reagent (sulfanilic acid and alpha naphthylamine in acetic acid)	1 ppm	<i>Z. anorg allgem. Chem.</i> 250, 321-30 (1943)
Cholak and McNary	A study of efficiency of different methods	Sensitivities compared	<i>J. Ind. Hyg. Toxicol.</i> 25, 354 (1943)
Averell and Others	Colorimetric standards based on sulfanilic acid and alpha-naphthylamine in acetic acid	5 ppm	<i>Anal. Chem.</i> 19, 1040 (1947)
Flagg and Lubene	NO <sub>2</sub> absorbed on silica gel Colorimetric with diphenylamine	1-50 ppm	<i>J. Ind. Hyg. Toxicol.</i> 30, 370 (1948)
Polezhaev and Girina	NO <sub>2</sub> sulfanilic acid and 1-naphthylamine	1 ppm	<i>Gigiena i Sanit</i> (1949) No. 11, 26-9

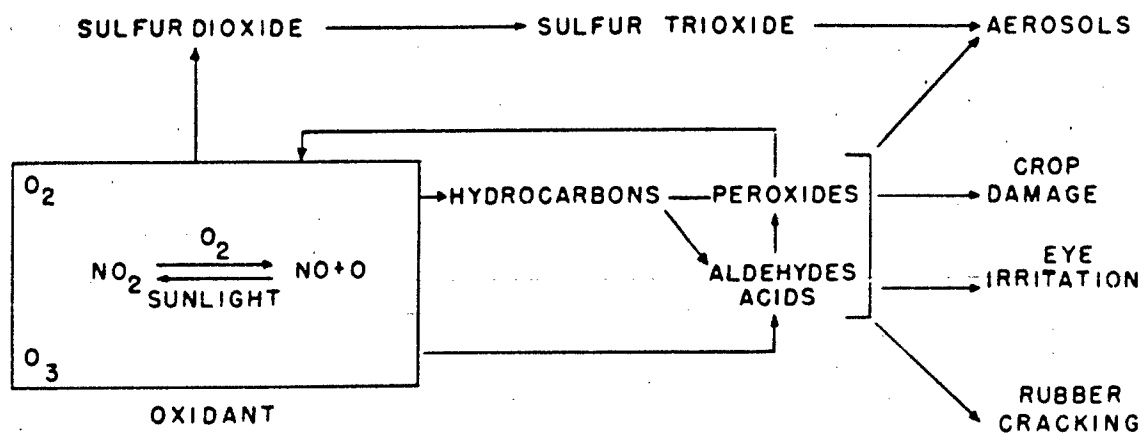
The fumes of nitrogen dioxide are frequently encountered in many industrial operations. In confined places, such as underground working and mines, small quantities of NO<sub>2</sub> may seriously impair the health of the worker. As a result of thousands of analytical tests made on a daily basis, the following correlation by Larson, Fischer and Hamming (1953) in the air over Los Angeles is significant:



	Periods of Good Visibility (7 miles)	Periods of Intense Smog
Concentration of Oxides of Nitrogen	ppm 0.08	ppm 0.4

While opinions of various workers differ greatly as to the toxic levels of  $\text{NO}_2$  vapors, the value set by the American Standards Association is 25 ppm (parts per million). In the Los Angeles area the nitrogen dioxide concentration reaches values of 0.4 ppm which is considerably less to the extent that their physiological effects can be noticed. The oxides of nitrogen are by-products of the combustion of some kinds of fuels, particularly by oxidation of ammonia waste gases from refineries which employ the regeneration of cracking catalysts, sulfuric acid manufacturing plants, pickling processes for stainless steels, and exhaust fumes from automobiles, trucks and buses, all contribute as sources of the oxides of nitrogen to air pollution. Estimates show that from combustion processes that nitrogen oxides are liberated at a rate of 200 to 300 tons daily into the Los Angeles air.

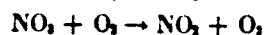
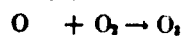
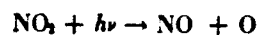
Haagen-Smit (1952) has made extensive investigations on photochemical reactions which occur during smog conditions. With the aid of the mass spectrograph, Haagen-Smit and coworkers were able to show that in the presence of oxides of nitrogen, functioning as catalysts, in the presence of sunlight a multitude of intermediate organic peroxides and ozone were formed through photochemical oxidation of alcohols, aldehydes, ketones, acids, and hydrocarbons such as are present in gasoline. A schematic diagram of reactions in polluted air leading to smog symptoms is shown in Figure 11.



From A. J. Haagen-Smit (*Ind. Eng. Chem.* 44, 1342 (1952)).

Fig. 11. Schematic presentation of reactions in which the oxides of nitrogen ( $\text{NO}$  and  $\text{NO}_2$ ) function as catalysts in the production of polluted air leading to smog symptoms.

The photochemical dissociation of nitrogen dioxide in the presence of sunlight provides a continuous source of atomic oxygen, while the regeneration of nitrogen dioxide by oxidation of the nitric oxide causes the reaction to be continuous. Blacet (1952) has postulated the following mechanism to account for the formation of atmospheric ozone from oxygen in the lower atmosphere.



It is significant to note that the photochemical reactions which lead to the formation of ozone by the catalytic action of nitrogen dioxide in the presence of sunlight and atmospheric pollutants are those which lead to the formation of complex intermediate compounds and peroxides which characterize the odor, eye irritation, and oxidation properties of smog effects. The oxides of nitrogen are, therefore, of immense importance in catalyzing the chain reactions leading to the formation of the detrimental substances during smog conditions. Even traces of the oxides of nitrogen while not present in concentrations capable of producing the syndrome observed during periods of intense smog are able to catalyze the formation of the noxious and toxic compounds present in smog.

## 2. ABSTRACTS

### 2.1 NITROUS OXIDE $\text{N}_2\text{O}$

1909

BAHR, EVA VON, "The Effect of Pressure on the Specific Absorption of Infrared Radiation by Gases," *Ann. Physik* 29, 780-96 (1909).

The author states that Beer's Law (absorption independent of density) was found not to hold for  $\text{CO}_2$ . This was observed by Angstrom. In the case of  $\text{CO}_2$  the specific absorption increases with density.

In order to test this exception to Beer's Law the following gases were investigated:  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{CS}_2$ ,  $\text{N}_2\text{O}$  and  $\text{NH}_3$ . It was shown by Eva Von Bahr that the absorption of a gas increases if the total pressure is increased by introducing a foreign gas which is transparent in the wavelength which is considered.

1926

LEIFSON, SIGMUND W., "Absorption Spectra of Some Gases and Vapors in the Schumann Region," *Astrophys. J.* 63, 73 (1926).

This is a study of the absorption in the Schumann region of a number of gases. They include: oxygen, nitrogen, nitrous oxide, hydrogen chloride, ammonia, methane, and water vapor. The instrumentation consisted of a vacuum grating spectrograph with an absorption cell with fluorite windows built into the discharge tube. The source of light was the continuous spectrum of hydrogen in the region  $\lambda\lambda$  2000-1600 Å and the secondary spectrum of hydrogen from  $\lambda\lambda$  1600 to 1250 Å.

The results obtained for oxygen, nitrogen, carbon monoxide, and carbon dioxide confirmed already existing data of previous investigators. New data were obtained for the remaining gases.

In regard to  $\text{N}_2\text{O}$  it is stated that nitrous oxide shows no selective absorption in the Schumann region. Two continuous bands were observed. The first extended from  $\lambda$  2000 to  $\lambda$  1680 Å, while the second was from  $\lambda$  1550 beyond the range of observation.

1927

JOSHI, S. S., "The Decomposition of Nitrous Oxide in the Silent Electric Discharge," *Trans. Faraday Soc.* 23, 227 (1927).

A detailed description of the apparatus and the preparation of nitrous oxide is given. The decomposition of nitrous oxide by the silent electric discharge was studied in the pressure range 11.0-82.0 cm Hg and 6000-12,500 volts.

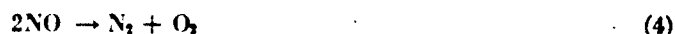
The decomposition goes to completion giving a mixture of nitrogen and oxygen. The nature of the final products is independent of the pressure and potential employed. Nitrogen peroxide occurs as an

intermediate product of the decomposition. The following mechanism was proposed for the formation of the nitrogen peroxide ( $\text{NO}_2$ ).

(a) Two simultaneous reactions (1) followed by (2).



(b) Three consecutive reactions (3), (4) and (5).



#### 1928

MACDONALD, JAMES Y., "The Photochemical Decomposition of Nitrous Oxide and Nitric Oxide," *J. Chem. Soc.* 1-14 (1928).

This is an excellent study of the decomposition of both nitrous and nitric oxides in light of wavelength from  $\lambda$  1860 Å to  $\lambda$  1990 Å. Nitric oxide was less thoroughly studied than nitrous oxide.

Nitrous oxide was shown to decompose according to the following general stoichiometric equation.



The following mechanisms were suggested for the decomposition of nitrous oxide according to equation (1).



The quantum efficiency was found to be  $3.9 \pm 0.2$  and does not change appreciably with temperature between  $0^\circ\text{C}$  and  $40^\circ\text{C}$ , nor with pressure up to about one atmosphere. The absorption coefficient increased  $1.47 \pm 0.05$  times for a  $10^\circ\text{C}$  rise in temperature.

In regard to nitric oxide, it was considered to decompose in two ways as follows.



Reaction (5) constituted about 90 per cent of the whole. Two possible mechanisms were suggested for the decomposition. The author states that insufficient evidence was obtained to warrant a decision.

Beer's absorption law was shown to hold strictly for both nitrous and nitric oxides. However, nitrous oxide absorbs light several times more strongly than nitric oxide.

Ten literature references are given to previous studies by other investigators.

#### 1929

JOSHI, S. S., "The Decomposition of Nitrous Oxide in the Silent Discharge. Part IV. Influence of the Addition of Foreign Gases," *Trans. Faraday Soc.* 25, 137 (1929)

The effect of the addition of nitrogen and oxygen on the ratio  $\text{N}_2/\text{O}_2$  was studied. An admixture of oxygen has a marked effect in increasing the ratio of nitrogen to oxygen in the final mixture.

## 1931

PLYLER, E. K., AND BARKER, F. F., "The Infrared Spectrum and the Molecular Configuration of  $N_2O$ ," *Phys. Rev.* 38, 1827 (1931)

The observations reported in this paper were upon the fundamental bands at  $17.0 \mu$ ,  $7.78 \mu$  and  $4.50 \mu$ .

Rotational analysis is given for the bands at  $17.0 \mu$ ,  $7.78 \mu$  and  $8.6 \mu$  which were resolved under high dispersion.

## 1932

DUTTA, ARUN K., "The Absorption Spectrum of Nitrous Oxide and the Heat of Dissociation of Nitrogen," *Proc. Roy. Soc. (London)*, A 138, 84 (1932).

A brief summary of previous investigations on the absorption spectrum of  $N_2O$  is given. Leifson (*Astrophys. J.*, 63, 73 (1926)) was the first to study the absorption spectrum of  $N_2O$ . Reference is also made to Wulf and Melvin (*Phys. Rev.* 39, 180 (1932)) who observed that radiation of  $\lambda$  2300 Å wavelength photochemically dissociated  $N_2O$  into NO and N, and also observed that  $N_2O$  had no band spectrum.

The author in the present investigation observed the absorption spectrum of  $N_2O$  in the quartz region with a small quartz spectrograph. The light source was a hydrogen discharge tube with aluminum electrodes run on a 2-kilowatt transformer. No band absorption was observed for  $N_2O$ . Continuous absorption was obtained beginning at  $\lambda$  2760 Å corresponding to 104.0 kcal.

VOLMER, M., AND FROELICH, H., "Thermal Decomposition of Nitrous Oxide," *Z. physik. Chem.* B 19, 85-88 (1932).

This is a continuation of the authors' work reported in *Z. physik. Chem.* B 10, 414-418 (1930). The temperature range was  $625^\circ$ - $680^\circ$ C, and the pressure between 2 and 300 mm Hg.

VOLMER, M., AND FROELICH, H., "Thermal Decomposition of Nitrous Oxide. Effect of Helium, Argon and Oxygen," *Z. physik. Chem.* B 19, 89-96 (1932).

This is a continuation of the work of Volmer in which the unimolecular character of the thermal dissociation of nitrous oxide was confirmed. The temperature range of the present study was between  $625^\circ$ C and  $670^\circ$ C, and the initial pressures of  $N_2O$  were about 1-50 mm Hg. The probabilities of activation per collision are given.

WULF, OLIVER R., AND MELVIN, EUGENE H., "The Dissociation of  $N_2O$  by Light, and the Electronic Levels of  $O_3$ ,  $N_2O$  and  $NO_2$ ," *Phys. Rev.* 39, 180 (1932).

This is an abstract of a paper read by the authors at the 173d regular meeting of the American Physical Society, University of Chicago, 27-28 November 1931. It is stated that nitrous oxide in long paths has shown no absorption over the spectral region  $\lambda$  10,500-2000 Å.

The authors report that absorption of radiation at  $\lambda$  2300 Å was observed. The absorption of this radiation led to the appearance of the  $\gamma$ -bands of NO. This was taken as evidence that absorption of this radiation led to dissociation of  $N_2O$  as follows.

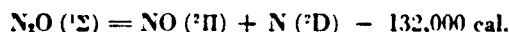


1934

HENRY, LOUIS, "Absorption Spectrum of Nitrous Oxide and Energy of Dissociation of Nitrogen," *Nature* 134, 498 (1934).

The author states that owing to the importance of the determination of nitrogen it seems of interest to report the dissociation energy of  $6.9 \pm 0.2$  volts obtained by the study of the absorption spectrum of  $N_2O$ .

The mechanism of the photochemical reaction is as follows.



The photochemical decomposition was studied by the radiations of a powerful cadmium spark filtered through layers of different concentrations of acetic acid.

HETTNER, G., POHLMANN, R., AND SCHUMACHER, H. J., "Die Struktur des Ozon-Molekuls und seine Banden im Ultrarot" ("The Structure of the Ozone Molecule and its Bands in the Infrared"), *Z. Phys.* 91, 372 (1934).

The  $7.6 \mu$  band which previously had been attributed to ozone,  $O_3$ , was shown to be due to  $N_2O_3$ .

HUNTER, E., "The Thermal Decomposition of Nitrous Oxide at Pressures up to 40 Atmospheres," *Proc. Roy. Soc. (London)* A 144, 386 (1934).

In this study it was shown that nitrous oxide up to pressures of 40 atmospheres and at temperatures up to  $900^\circ \text{C}$  thermally decomposes according to the following equations.



The measured pressure increase will correspond to the stoichiometric equation.



SEN GUPTA, P. K., "Fluorescent Radiation from  $N_2O$ ," *Proc. Roy. Soc. (London)* A 146, 824 (1934).

The author states that experimental data so far collected indicate that under the action of light quanta of suitable wavelength,  $N_2O$  dissociates into a normal NO and N which may be in different excited metastable states.

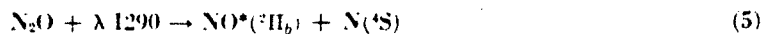


The energies corresponding to  $h\nu_1$ ,  $h\nu_2$ , and  $h\nu_3$  are given for absorption beginning at wavelengths  $\lambda$  2750 Å,  $\lambda$  1850 Å, and  $\lambda$  1580 Å, respectively. So far no evidence of the production of an excited NO molecule as a result of light absorption has been obtained, according to the reaction,



An explanation is given to show why absorption corresponding to mechanism (4) is not obtained. The calculated value for  $h\nu_4$  is 223.4 kcal corresponding to the wavelength  $\lambda$  1290 Å which would lie almost at the limit of the fluorite spectrograph.

Experimental details are given for obtaining evidence for the following photochemical mechanism.



SEN GUPTA, P. K., "The Absorption Spectrum of  $\text{N}_2\text{O}$  in the Schumann Region," *Bull. Acad. Sci., United Province Agra Oudh, India* 3, 197 (1934).

The spectral region studied was from 1330 Å to 2200 Å. The instrumentation was a fluorite prism spectrograph with a hydrogen tube as light source. The gas was contained in a cell of 10 centimeters length with fluorite windows. The pressure range was from 0.5 to 20 cm Hg.

$\text{N}_2\text{O}$  was found to absorb light at a wavelength of  $\lambda 1850$  Å, to transmit at about  $\lambda 1700$  Å, and again to absorb light at  $\lambda 1580$  Å. The absorption was considered to be due to the photochemical decomposition of  $\text{N}_2\text{O}$  according to the following reaction mechanism.



SEN GUPTA, P. K., "Absorption Spectra of Molecules," *Z. physik* 88, 647-660 (1934).

From a study of the shape of the Franck-Condon curves the continuous absorption of  $\text{N}_2\text{O}$  shows regions of absorption separated by regions of transmission. Absorption occurs in the regions of the following wavelengths:  $\lambda 2750$  Å,  $\lambda 1850$  Å, and  $\lambda 1580$  Å. The mechanisms for dissociation are the same as given in former papers by the author.

VOLMER, M., AND BRISKE, H., "The Decomposition of Nitrous Oxide," *Z. physik. Chem. B* 25, 81-89 (1934).

This is an extension of Volmer's former work on the thermal decomposition of nitrous oxide. In this theoretical discussion the effects of the decomposition products on the course of the reaction are taken into consideration.

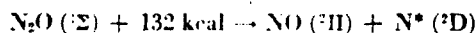
#### 1935

HENRY, LOUIS, "Photochemical Decomposition of Nitrous Oxide and Dissociation Energy of Nitrogen," *Compt. rend.* 200, 656 (1935).

It was found that absorption begins at a higher wavelength as the temperature increases. At  $20^\circ\text{C}$  absorption begins at  $\lambda 2246$  Å, while at  $675^\circ\text{C}$  it begins at  $\lambda 2604$  Å.

By plotting wavelength against temperature and extrapolating to zero degree Kelvin the minimum energy required to activate  $\text{N}_2\text{O}$  was found to be 132 kcal.

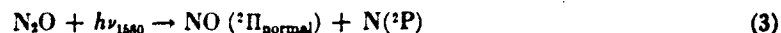
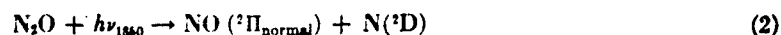
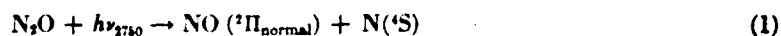
Assuming that the dissociation of  $\text{N}_2\text{O}$  is according to the following mechanism,



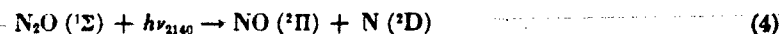
the dissociation energy of nitrogen,  $D_{\text{N}_2}$ , was calculated to be 158 kcal.

SEN GUPTA, P. K., "Photodissociation of Nitrous Oxide," *Nature* 136, 513 (1935).

A brief summary is given of previous work by Wulf and Melvin (*Phys. Rev.* 39, 180 (1932), Dutta (*Proc. Roy. Soc. (London)* A 138, 84 (1932)), and the present author, Sen Gupta (*Bull. Acad. Sci. U. P.* 3, 197 (1934)). The results show the absorption of light by  $\text{N}_2\text{O}$  to take place according to the following mechanisms.



Reference is made to the remeasurement of the absorption spectrum of nitrous oxide at different temperatures by Henry (*Nature* 134, 498 (1934)) who assumed the following process for dissociation of  $\text{N}_2\text{O}$ .



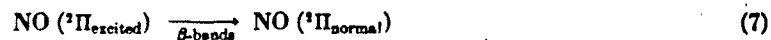
This photochemical mechanism explained both the diamagnetism of  $\text{N}_2\text{O}$  (giving a  $^1\Sigma$  state, and also a value of  $6.9 \pm 0.2$  volts for the heat of dissociation of  $\text{N}_2$ ). The present (1935) accepted value  $D_{\text{N}_2}$  is 7.34 volts given by Herzberg and Sponer.

Sen Gupta gives reasons for doubting the photochemical dissociation mechanism of Henry in the quartz region. Sen Gupta found that when  $\text{N}_2\text{O}$  is irradiated by light having the short-wave limit at  $\lambda$  1200 Å, the  $\beta$ -bands of NO comes out in fluorescence. The  $\beta$ -bands were accounted for as follows.

By absorption:



By fluorescence:



The excitation energy of the  $\beta$ -bands is 128.8 kcal, so that  $h\nu_2 - h\nu_1 = 128.8$  kcal. If by Henry's explanation,  $h\nu_1$  corresponds to 2140 Å,  $h\nu_2$  would have a value of 262.4 kcal corresponding nearly to  $\lambda$  1090 Å. As a result light of wavelength greater than  $\lambda$  1090 should not be able to excite the  $\beta$ -bands. Excitation can be produced by  $\lambda$  1200 Å. If  $h\nu = \lambda$  2750 Å, then  $h\nu_2 = \lambda$  1250 Å.

#### 1936

DUNCAN, A. B. F., "The Far Ultraviolet Absorption Spectrum of  $\text{N}_2\text{O}$ ," *J. Chem. Phys.* 4, 638 (1936).

In the research work reported in this paper the author states that the absorption spectrum of  $\text{N}_2\text{O}$  was reinvestigated from 2200 Å down to 850 Å, the limit of observation. No bands were found below 997 Å.

The spectra were photographed with a 120,000-line, 1-meter focus, glass grating used at normal incidence. The light source was the Lyman continuum with hydrogen as the conducting gas. In a few cases purified helium was used. The pressure of the  $\text{N}_2\text{O}$  was varied from 0.001 to 0.53 mm Hg. The spectrograph served as the absorbing column. Evidence from a Rydberg series indicated that the photoionization of  $\text{N}_2\text{O}$  is 12.66 ev.

#### 1937

NOYES, W. ALBERT, JR., "Photochemical Studies. XXV. The Direct Photochemical Decomposition of Nitrous Oxide," *J. Chem. Phys.* 5, 807-812 (1937).

In this report the author has described his studies on the decomposition of nitrous oxide. An aluminum spark in air was used as light source. The wavelength was greater than 1850 Å corresponding to about 6.7 ev., however the absorption extended to about 2300 Å, equivalent to about 5.4 ev. The experimental details are described.



The number of molecules of gas (uncondensed by the liquid air employed in the experiments) formed per quantum absorbed by  $N_2O$  was determined. The study was made both with the presence and absence of mercury vapor. The primary dissociation processes and subsequent reactions are given in part by the following mechanism.



Additional reaction mechanisms are given, and speculations of the electronic states.

1938

ADEL, ARTHUR, AND LAMPLAND, C. O., "A New Band in the Absorption Spectrum of the Earth's Atmosphere," *Astrophys. J.* 87, 198 (1938).

The major absorption bands in the spectrum of the earth's atmosphere are due to water vapor, carbon dioxide and ozone constituents. The following table is the interpretation of the far-infrared telluric spectrum.

Band ( $\mu$ )	Absorbing Molecules	Band Designation
14.97	$CO_2$	$\nu_2$
14.1	$O_3$	—
9.6	$O_3$	—
7.6	$N_2O_2$	—
6.3	$H_2O$	$\nu_2$
4.7	$O_3$	—
4.3	$CO_2$	$\nu_2$
3.2	$H_2O$	$2\nu_2$

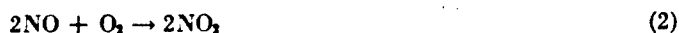
The band at  $7.6 \mu$  in the spectrum of the atmosphere is announced in the present paper. This band can not be traced to the spectra of water vapor, carbon dioxide or ozone. The spectrum of pure ozone in quantities in excess of the amount in the ozonosphere does not give this band. Since the energy level diagram of the  $CO_2$  is well known there is no transition at  $7.6 \mu$ . The energy level diagram of water vapor similar to that of carbon dioxide does not provide a suitable transition.

The new band at  $7.6 \mu$  is attributed to a hitherto unrecognized atmospheric constituent. The molecule  $N_2O_2$  is found as a common impurity of ozone. The infrared spectrum of ozone nearly always shows a strong band at  $7.6 \mu$  which was considered to be a member of the ozone spectrum. In order to account for the minute traces of  $N_2O_2$  in the ozonosphere the following reactions are suggested and considered to be reasonably expected.



This reaction is known to occur by the action of electrical discharges or ultraviolet radiation upon mixtures of nitrogen and oxygen.

In the presence of oxygen the following reaction results.



In the presence of ozone nitrogen dioxide yields nitrogen pentoxide.



By comparing the intensity of absorption at  $7.6 \mu$  in the solar prismatic spectrum with the intensity of absorption from results obtained by Hettner, Pohlmann and Schumacher (*Z. Phys.* 91, 372 (1934)), the authors estimate there is one molecule of  $\text{N}_2\text{O}_5$  for every hundred molecules of  $\text{O}_3$  present in the ozonosphere.

Small quantities of the following oxides of nitrogen,  $\text{NO}$ ,  $\text{N}_2\text{O}$ ,  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$ , are to be expected in the upper atmosphere as a result of the photochemistry of nitrogen-oxygen mixtures. However, none of these have absorption bands at  $7.6 \mu$  which favors the argument that the new band at  $7.6 \mu$  is due to atmospheric  $\text{N}_2\text{O}_5$ .

ADEL, ARTHUR, "Further Detail in the Rock Salt Prismatic Solar Spectrum," *Astrophys. J.* 88, 186 (1938).

In the spectral region from  $7.2 \mu$  to  $8.5 \mu$  with increased resolving power additional detail in the rock-salt prismatic solar spectrum was disclosed in the vicinity of the diverging wall of the great water band  $\nu_2$ .

It is pointed out that these new bands may indicate the existence of additional oxides of nitrogen in the atmosphere. The  $\text{N}_2\text{O}$  molecule has two doublet bands with centers at  $7.77$  and  $8.5 \mu$ , the  $7.77$  being more than twice as intense. The latter observation was made by Plyler and Barker (*Phys. Rev.* 38, 1827 (1931)).

The author suggests that the R branch of the  $\text{N}_2\text{O}$  band at  $7.77 \mu$  and the  $\text{N}_2\text{O}_5$  band at  $7.6 \mu$  combine to form the telluric absorption with the center at  $7.63 \mu$ .

DUFFIEUX, P. MICHEL, "Oxides of Nitrogen in the Atmosphere," *Bull. Soc. Sci., Bretagne* 15, 228 (1938).

The author states that the lack of spectroscopic indications of the oxides of nitrogen in the upper atmosphere is not conclusive evidence of their absence.

HENRIQUES, F. C., DUNCAN, A. B. F., AND NOYES, W. ALBERT, JR., "Photochemical Studies. XXVII. The Effect of Radiation on Mixtures of Nitrogen Dioxide and Nitrous Oxide and its Relationship to the Photochemical Decomposition of Nitrous Oxide," *J. Chem. Phys.* 6, 518-522 (1938).

In this report upon the photochemical decomposition of nitrous oxide the authors conclude that two primary processes are necessary to explain the direct photochemical decomposition of  $\text{N}_2\text{O}$ .



Reaction (2) must be followed by reaction (3).



The latter reaction (3) is necessary to explain previously determined quantum yields. The authors state that the energy of activation of reaction (3) is probably less than 10,000 cal.

The experimental method employed in the investigation is described in detail. Two light sources and reaction vessels were used in order to determine possible separate effects due to  $^3\text{P}$  and  $^1\text{D}$  oxygen atoms.

The light sources were (a) a General Electric type H 3 mercury lamp, and (b) a cadmium spark operated at 2 kva, 25,000 volts from which radiation between 2150 Å and 2350 Å was isolated by filters.

There is a comprehensive discussion of the results obtained. Nine literature references are included of previous investigations by other workers.

## 1939

ADEL, ARTHUR, "Atmospheric Absorption of Infrared Solar Radiation at the Lowell Observatory," *Astrophys. J.* 89, 1 (1939).

This is the first of a series of papers by Adel describing the degree of absorption by the earth's atmosphere of infrared radiations. In this paper the continuous absorption due to the pure rotation spectrum of the water-vapor molecule is considered. No data on the absorption spectrum of the oxides of nitrogen are included.

ADEL, ARTHUR, "Note on the Atmospheric Oxides of Nitrogen," *Astrophys. J.* 90, 627 (1939).

Attention is called to Figure 1 in the paper which appears to indicate that the recently discovered atmospheric band associated with the long wavelength of water vapor is produced by joint absorption of nitrous oxide ( $N_2O$ ) and nitrogen pentoxide ( $N_2O_5$ ).

Two curves are shown in Figure 1. One was obtained from a relatively dry atmosphere with the sun as source and the atmosphere as the absorbing medium. The other curve was produced by radiation from a Nernst glower, passing a layer of 1 cm of nitrous oxide at atmospheric pressure combined with the short air path in the spectrometer.

The  $7.77 \mu$  band of nitrous oxide appeared to match the atmospheric band. There is also a shallow nitrous oxide band at  $8.7 \mu$  matched by a weak atmospheric band. The short wavelength trough of the atmospheric band at  $7.77 \mu$  somewhat displaced and broadened as compared with nitrous oxide absorption at  $7.77 \mu$ . This suggested possible absorption by nitrogen pentoxide at  $7.6 \mu$ .

The observations reported in the paper of the  $7.77 \mu$  and  $8.57 \mu$  bands indicate that there is an  $N_2O$  layer comparable to the ozone layer in the upper atmosphere which may be equivalent to several millimeters at atmospheric pressure in extent.

## 1940

ADEL, ARTHUR, AND LAMPLAND, C. C., "Atmospheric Absorption of Infrared Solar Radiation at the Lowell Observatory. II. The Spectral Interval:  $5.8-8.0 \mu$ ," *Astrophys. J.* 91, 1 (1940).

This is the second of a series of papers of the absorption spectrum of the earth's atmosphere. The spectral region considered is from  $5.5 \mu$  to  $8.0 \mu$ .

The principal features of this spectral range are (1) the great water-vapor band which possesses a long base of zero transmission, and (2) the absorption bands due to the oxides of nitrogen, possibly nitrous oxide ( $N_2O$ ) and nitrogen pentoxide ( $N_2O_5$ ). This band of oxides of nitrogen is contained in the long-wavelength or diverging wall of the water-vapor band.

Six graphs of solar intensity as a function of wavelength are shown. They are arranged to indicate the progressive change corresponding to diminishing water-vapor content of the atmosphere within the spectral

range  $5.5 \mu$  to  $8.0 \mu$ . The region from  $8.0 \mu$  to  $11.0 \mu$  is also included which is to be discussed in succeeding papers of the present series.

ADEL, ARTHUR, AND TAMPLAND, C. O., "Atmospheric Absorption of Infrared Solar Radiation at the Lowell Observatory. III and IV. The Spectral Intervals:  $8.0-11.0 \mu$  and  $11.0-14.0 \mu$ ," *Astrophys. J.* 91, 481 (1940).

This paper contains the discussion of the degree of absorption of infrared radiations as a consequence of the absorption spectrum of the earth's atmosphere. A brief summary of the series of papers is given. In the first paper designated as Part I, the continuous absorption spectrum of the atmosphere is considered. This is governed mainly by water vapor.

The second paper, Part II, is concerned with the spectral region  $5.5-8.0 \mu$ . The absorption in this spectral range is due to water vapor and the oxides of nitrogen. In the present paper, the third of the series, the spectral regions III and IV are defined.

The region from  $8.0 \mu$  to  $11.0 \mu$  is designated as region III. The transmission in this spectral range is determined by water vapor and ozone.

In region IV from  $11.0 \mu$  to  $14.0 \mu$  the transmission is due to water vapor and carbon dioxide.

NICOLLE, JACQUES, AND VODAR BORIS, "Ultraviolet Absorption Spectrum of Nitrous Oxide at  $+20^\circ\text{C}$  and  $-90^\circ\text{C}$ ," *Compt. rend.* 210, 142 (1940).

The authors report their investigation of the ultraviolet absorption of  $\text{N}_2\text{O}$  at two different temperatures  $+20^\circ\text{C}$  and  $-90^\circ\text{C}$ . The pressures were from 100 to 760 mm Hg and the column thickness 70-574 cm. The absorption was independent of pressure, and was less at  $-90^\circ\text{C}$  than at  $+20^\circ\text{C}$ .

At  $-90^\circ\text{C}$  the origin of the absorption was at  $\lambda 2350 \text{ \AA}$ . The investigation indicated that the absorption region studied was only one of the branches reported by Duncan (1936), the band with a center at approximately  $\lambda 1900 \text{ \AA}$ . Reference is also made to the results of Plyler and Barker (1931).

SPONER, H., AND BONNER, L. G., "Note on the Continuous Absorption of  $\text{N}_2\text{O}$ ," *J. Chem. Phys.* 8, 33 (1940).

In the introduction of this paper reference is made to the previous investigations of ultraviolet absorption. Thirteen references are included of this previous work. The authors discuss the results of their experiments on the dissociation of  $\text{N}_2\text{O}$  in the long wavelength of the near ultraviolet. Various dissociation products and possible electronic states for dissociation processes of  $\text{N}_2\text{O}$  are listed in Table I of the paper.

Dissociation Processes and Possible Electronic States of  $\text{N}_2\text{O}$

	Energy Required, Volts
1. $\text{N}_2\text{O} \rightarrow \text{O}^+\text{P} + \text{N}_2$	1.71
2. $\text{N}_2\text{O} \rightarrow \text{O}^+\text{D} + \text{N}_2$	3.68
3. $\text{NO}^+\text{H} + \text{N}^+\text{S} + \text{H}$	3.77
4. $\text{N}_2\text{O} \rightarrow \text{O}^+\text{S} + \text{N}_2$	5.90
5. $\text{NO}^+\text{H} + \text{N}^+\text{D} + 2^+\text{H}, 2^+\text{H}, 1^+\text{D}$	6.15
6. $\text{NO}^+\text{H} + \text{N}^+\text{P} + 2^+\text{H}, 2^+\text{H}, 1^+\text{D}$	7.13
7. $\text{N}_2\text{O} \rightarrow \text{O}^+\text{P} + 1^+\text{H}, 1^+\text{H}$	7.84
8. $\text{N}_2\text{O} \rightarrow \text{O}^+\text{P} + 2^+\text{H}, 2^+\text{H}, 1^+\text{D}$	9.0
9. $\text{NO}^+\text{S} + \text{N}^+\text{S} + \text{S}$	9.2
10. $\text{NO}^+\text{S} + \text{N}^+\text{S} + \text{H}$	9.4
11. $\text{NO}^+\text{S} + \text{N}^+\text{D} + 1^+\text{H}, 1^+\text{H}, 1^+\text{D}$	11.6
12. $\text{NO}^+\text{H} + \text{N}^+\text{D} + 2^+\text{H}, 2^+\text{H}, 1^+\text{D}$	11.8

1941

ADEL, ARTHUR, "The Grating Infrared Solar Spectrum. II. Rotational Structure of the Nitrous Oxide (NNO) Band  $\nu_1$  at  $7.78 \mu$ . *Astrophys. J.* 93, 509 (1941).

The identification and existence of an atmospheric layer of nitrous oxide was established by Adel in 1939. This was accomplished by comparing the solar prismatic spectrum with the prismatic spectrum of nitrous oxide.

In this note the grating solar spectrum is compared with the grating spectrum of nitrous oxide. Figure 3 in the paper shows the negative branch of  $\nu_1$  (NNO) as obtained by approximately 1 cm (NNO) at N.T.P. Figure 2 in the paper shows the grating solar spectrum.

The comparison of the two grating spectra identifies atmospheric nitrous oxide. The rotational structure of  $\nu_1$  (NNO) may be observed in the complex background of the solar spectrum due to other components of the atmosphere.

ADEL, ARTHUR, "The Grating Infrared Solar Spectrum VI. The Map from  $14 \mu$  to  $7 \mu$ . *Astrophys. J.* 94, 451 (1941).

Some 400 absorption lines are shown in the map. An extensive table of wavelengths and frequencies are included for the spectral range  $14 \mu$  to  $7 \mu$ .

The long wavelength slope of the great water band including the rotational lines of  $\nu_1$  of  $N_2O$  is contained in Figures 30-36. In all 36 figures are included.

ADEL, ARTHUR, "Equivalent Thickness of the Atmospheric Nitrous Oxide Layer," *Phys. Rev.* 59, 944 (1941).

In a paper read at the Washington Meeting of the American Physical Society 1-3 May 1941, the author states that atmospheric nitrous oxide is presumably at a high level, and that it has a photochemical origin.

Its infrared absorption bands appear to remain of nearly uniform strength throughout the seasons. The fine structure of the  $\nu_1$  band of atmospheric nitrous oxide at  $7.78 \mu$  was studied by employing a 2400-line echelette grating.

By comparing the atmospheric absorption with controlled experiments on the absorption of nitrous oxide in the laboratory 3 mm of the gas (NTP) has the same absorption in  $\nu_1$  as the atmospheric layer.

Since the infrared absorption of nitrous oxide is pressure sensitive this value is a lower limit. At the reduced pressures in the upper atmosphere far more gas would be required to yield the same effect.

1942

KELLNER, LOTTE, "The Infrared Absorption of Atmospheric Gases," *Quart. J. Roy. Meteorol. Soc.* 68, 204 (1942).

Diatomic molecules which possess no permanent dipole moment do not absorb infrared light. Thus oxygen, nitrogen and hydrogen are transparent in the infrared. Triatomic and polyatomic molecules such

as  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{O}_3$ , and the various oxides of nitrogen show strong absorption bands in the spectral region from  $1\ \mu$  to  $18\ \mu$ .

The oxides of nitrogen,  $\text{N}_2\text{O}$ ,  $\text{NO}$  and  $\text{NO}_2$ , show great intensity of absorption as compared with  $\text{H}_2\text{O}$ . Even small traces of  $\text{CO}_2$ ,  $\text{O}_3$ , and  $\text{N}_2\text{O}$  in particular affect the absorption spectrum of the atmosphere.

SUTHERLAND, G. B. B. M., "Detection of Small Traces of Non-Rare Gases in the Atmosphere by Infrared Spectra," *Quart. J. Roy. Meteorol. Soc.* 68, 213 (1942).

This paper contains the conclusions from the survey of the data on the absorption of infrared radiation by gases in the atmosphere, other than water vapor. The absorption spectrum of the atmosphere exhibits 25 bands between  $0.7\ \mu$  and  $14.0\ \mu$ . Most of these are satisfactorily accounted for by the presence of  $\text{H}_2\text{O}$ ,  $\text{CO}_2$  and  $\text{O}_3$ . The author states that the quantitative aspect of these absorptions are only partially understood because accurate laboratory measurements of the requisite absorption coefficients are lacking.

With reference to  $\text{N}_2\text{O}$  there is good evidence that nitrous oxide is responsible for the absorption superimposed on the water vapor absorption between  $7\ \mu$  and  $8\ \mu$ . Sutherland states that Adel's suggestion that at least part of this absorption was due to  $\text{N}_2\text{O}$  is not substantiated by Adel's more recent work.

The possibility of the existence of the following gases and their detection through their infrared absorptions were considered:  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ ,  $\text{CH}_3\text{O}$ ,  $\text{H}_2\text{S}$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{HCN}$ ,  $\text{C}_2\text{N}_2$ ,  $\text{NH}_3$ .

From laboratory data on the absorption coefficients, there is indication that the amounts of the order of one centimeter atmosphere of most gases could be present and would have escaped detection in the infrared because of lack of resolving power employed between  $2\ \mu$  and  $7\ \mu$ , and partly because the key absorption bands are overlaid by intensely strong bands of  $\text{H}_2\text{O}$  and  $\text{CO}_2$ .

WILDT, RUPERT, "The Geochemistry of the Atmosphere and the Constitution of the Terrestrial Planets," *Rev. Mod. Phys.* 14, 151 (1942).

This paper is a discussion of the geochemistry of the following terrestrial planets: Venus, Mars, Mercury, and the Moon. Since the atmosphere of the earth, due to absorption by  $\text{O}_3$ , is opaque to radiation shorter than about 2900 Å, the characteristic absorption spectra of nitrogen and the noble gases are hidden from the observer.

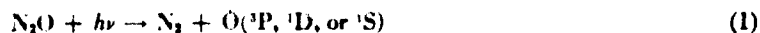
A brief reference is made to Adel's discovery (*Astrophys. J.* 90, 626 (1939); 93, 506, 509 (1941); 94, 375, 379, 449 and 451 (1941)) of  $\text{N}_2\text{O}$  in the earth's atmosphere as the result of a painstaking analysis of the infrared solar spectrum.

#### 1943

BAMFORD, C. H., "Photochemical Processes in an Oxygen-Nitrogen Atmosphere," *Reports Prog. Phys.* 9, 75 (1942-1943).

Nitrous Oxide ( $\text{N}_2\text{O}$ ) has two regions of continuous absorption. One is in the 2200 Å to 1700 Å region, and the other begins at 1580 Å and extends far down into the ultraviolet. It is pointed out that the earliest photochemical studies of nitrous oxide was that of Macdonald (1928), who employed light of  $\lambda\lambda$  1990-1860 Å. The nitrous oxide was observed to decompose into nitrogen, oxygen and nitric oxide. The quantum efficiency of decomposition was 3.9 (molecules  $\text{N}_2\text{O}$  per quantum).

Noyes (1937) studied the following processes.



Process (1) may be followed by



The following reactions may be expected to follow reaction (2).



The general conclusion is that process (2) seems probable, but its occurrence is not regarded as definitely proved.

PRICE, W. C., "Absorption Spectra and Absorption Coefficients of Atmospheric Gases," *Reports Prog. Phys.* 9, 10 (1942-1943)

This is a report on the electronic spectra and coefficients of the atmospheric gases. In a previous report by Chapman and Price (*Reports Prog. Phys.* 3, 55 (1936)) the data on the more common constituents of the atmosphere were reviewed. In the present report the spectra of the oxides of nitrogen are considered in detail because of the recent identification of  $\text{N}_2\text{O}$  and  $\text{N}_2\text{O}_2$  bands in the infrared Fraunhofer spectrum by Adel (1939).

A survey of the following gases is given:  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ -vapor,  $\text{H}_2\text{O}_2$ ,  $\text{O}_3$ , and the oxides of nitrogen ( $\text{N}_2\text{O}$ ,  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{O}_3$ ,  $\text{N}_2\text{O}_4$ ,  $\text{NO}_3$ ),  $\text{H}_2\text{S}$ ,  $\text{NH}_3$ , saturated hydrocarbons, formaldehyde, and sulfur dioxide.

#### Nitrous Oxide, $\text{N}_2\text{O}$ .

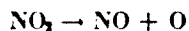
According to Sutherland nitrous oxide may be present in the atmosphere to the amount equivalent to a thickness of 1 cm of the gas at S. T. P. Exceedingly long path lengths and relatively high pressures are required to detect absorption in nitrous oxide at wavelengths greater than 2000 Å. Due to this transparency nitrous oxide is considered to be relatively stable photochemically. This high transparency is associated with its closed-shell electronic structure.

A brief survey of absorption measurements of nitrous oxide from  $\lambda\lambda$  3065 Å to 1350 Å is given. It is stated that direct photochemical work on nitrous oxide shows the presence of  $\text{NO}$ ,  $\text{O}_2$  and  $\text{NO}_2$  among the products of photodissociation.

#### Nitric Oxide, $\text{NO}$ .

Since nitric oxide,  $\text{NO}$ , is formed from  $\text{N}_2\text{O}$  by photodissociation and by reaction of  $\text{N}_2\text{O}$  molecules with oxygen atoms in the presence of a third body it may be an important constituent of the atmosphere.

The formation of  $\text{NO}$  from  $\text{NO}_2$  by the following equation is considered likely because of high light intensities during the day and low pressures.



A brief survey of the absorption spectra of NO is given. This includes the investigations of Leifson (1926), Flory and Johnston (1935), and Lambrey (1929).

#### *Nitrogen Dioxide, NO<sub>2</sub>.*

The absorption of nitrogen dioxide from 6000 Å to shorter wavelengths was shown by Curry and Herzberg (1933). Reference is also made to the work of Harris, King, Benedict and Pearse (1940), to Price and Simpson (1941), and Dixon (1942). These determinations would seem to limit the amount of nitrogen dioxide present in the upper atmosphere during the day to less than 0.1 mm. Photodissociation into nitric oxide would reduce this quantity to a very low value.

The author states that if much nitric oxide is present in the upper atmosphere some nitrogen dioxide might be formed during the night. This would be shown by Fraunhofer absorption during the brief interval of sunrise, or in the spectrum of the moon. Since the formation of nitrogen dioxide from nitric oxide and oxygen atoms is a termolecular reaction, the reaction would be very slow at low pressures. Thus a considerable amount of nitric oxide might yield only a very small quantity of nitrogen dioxide.

#### *Nitrogen Pentoxide, N<sub>2</sub>O<sub>5</sub>.*

The work of Jones and Wulf (1937) is mentioned. These investigators give absorption coefficients for nitrogen pentoxide. However, the absence of discrete bands would prevent their values to be used to set a limit on the quantity of N<sub>2</sub>O<sub>5</sub> that might be present in the atmosphere.

#### *Nitrogen Trioxide, NO<sub>3</sub>.*

From absorption coefficient measurements by Sprenger (1931) the limit of the amount of this gas in the atmosphere would be considerably less than an equivalent thickness of 0.1 mm at S. T. P.

SUTHERLAND, G. B. B. M., AND CALLENDAR, G. S., "The Infrared Spectra of Atmospheric Gases other than Water Vapor," *Reports Prog. Phys.* 9, 18 (1942-1943).

The generally accepted interpretation of atmospheric absorption in the infrared is shown in Figure 1 in the paper. It is noticed that below 7 μ all absorptions with the exception of the electronic O<sub>2</sub> band at 0.76 μ are due to H<sub>2</sub>O, CO<sub>2</sub>, and O<sub>3</sub>. At 7.6 μ and 7.8 μ there are two weak bands attributed to N<sub>2</sub>O<sub>5</sub> and N<sub>2</sub>O respectively.

The definition of absorption is given. In the equation for Lambert-Beer's Law

$$I_{\lambda} = I_{0\lambda} e^{-k_{\lambda}d} = I_{0\lambda} e^{-k_{\lambda}q}$$

where  $I_{\lambda}$  is the intensity of the transmitted radiation between  $\lambda$  and  $\lambda + \delta\lambda$ .

$I_{0\lambda}$  the intensity of the incident radiation between  $\lambda$  and  $\lambda + \delta\lambda$ .  $c$  is the concentration, i.e. number of absorbing molecules per unit path length.

$l$  the path length of the radiation in the absorbing gas.

$q$  the path length in centimeters which would contain the same number of molecules if the gas were at S. T. P.

Chapman proposed the name atmo-centimeter as the unit for this quantity.



### *Nitrous Oxide and Nitrogen Pentoxide.*

Reference is made to the work of Adel and Lampland (1938) who showed that the two weak bands at  $7.6 \mu$  and  $7.8 \mu$  were due to the presence of appreciable quantities of  $N_2O_5$  and  $N_2O$  respectively in the atmosphere. Later Adel (1939) considered these bands as a doublet due primarily to  $N_2O$ , but having the shorter wave maximum intensified by the presence of  $N_2O_5$ . Further evidence for the presence of  $N_2O$  in the atmosphere was the discovery of an additional weak absorption band at  $8.6 \mu$  which was assigned to  $N_2O$ . Employing a grating spectrometer Adel (1941) announced the identification of the individual rotation lines of  $N_2O$  in the spectrum of the atmosphere at  $7.7 \mu$ .

Sutherland and Callendar in the present paper found a value of 0.8 for the absorption coefficient,  $k_\lambda$  of the  $7.8 \mu$  band of  $N_2O$ . From this they estimated that there were 0.8 atmo-cm of  $N_2O$  in the atmosphere. Taking this value with the computed figure for  $k_\lambda$  (0.3) of the  $N_2O$  band at  $8.6 \mu$ , the latter band was inferred to have an average absorption intensity of 20 per cent. The uncertainties in these values seem too great to draw any conclusion.

The case of  $N_2O_5$  is also considered. In the summary it is stated that there is fairly good evidence for a few millimeters of  $N_2O$  in the atmosphere and very weak evidence for a few tenths of a millimeter of  $N_2O_5$ .

### 1944

HUTCHINSON, G. EVELYN, "Nitrogen in the Biochemistry of the Atmosphere," *Am. Scientist* 32, 178 (1944).

This paper is an extensive summary of the quantitative estimate of the rate at which nitrogen undergoes certain phases of its cyclical geochemical migration into and out of the atmosphere. The following table is included on the estimated distributed nitrogen in the earth.

In primary lithosphere	~ 37,000 gm per cm <sup>2</sup>
In atmosphere	755 gm per cm <sup>2</sup>
In sediments	87 gm per cm <sup>2</sup>

The sources of combined nitrogen in rain and snow are:

- (a) From soil and the ocean
- (b) From fixation of atmospheric nitrogen
  - 1. Electrically
  - 2. Photochemically
  - 3. In the trail of meteorites
- (c) From industrial contamination

The following topics are discussed in the paper

- (1) Biological fixation of nitrogen
- (2) Bacterial regulation of the composition of the atmosphere
- (3) Speculations on the evolution of the nitrogen cycle

KRIEGL, MONROE W., "Analysis for Hydrocarbons in the Presence of Nitrous Oxide," *Geophys.* 9, 447 (1944).

This paper describes the technique for the analysis of soil air for small quantities of hydrocarbons. There are reasons for believing that nitrous oxide exists in soil air.

The boiling point of nitrous oxide places it in the light hydrocarbon fraction. The reasons for believing that nitrous oxide is a constituent of soil air are given. A table of boiling points of gases at one atmosphere after Hodgman and Holmes, "Handbook of Chemistry and Physics," 26th ed., Cleveland, Ohio, The Chemical Rubber Publishing Co. (1942) is included. Nitrous oxide has a boiling point of  $-89.5^{\circ}\text{C}$  at 760 mm Hg pressure.

The dissociation of nitrous oxide in the silent discharge at pressures above 10 cm Hg was investigated by Joshi (*Trans. Faraday Soc.* 23, 227 (1927); *ibid.* 25, 137 (1929)). The dissociation was found by Joshi to be according to the following reactions.



A plausible source of nitrous oxide in soil air is suggested as the slow decomposition of commercial fertilizers, especially in farming regions. The element nitrogen is present in the form of ammonium salts, nitrites or nitrates in fertile soils. Pure nitrous oxide is prepared by the gentle heating of ammonium nitrate.



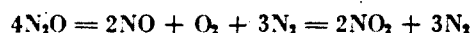
Studies of decomposition of vegetation under aerobic conditions show that nitrous oxide forms a large portion of the condensed gas fraction.

Details are given for the analysis of hydrocarbon gases in the presence of nitrous oxide. The method seemed to be satisfactory at the Laboratories of the Carter Oil Company, Tulsa, Oklahoma:

#### 1945

BRINER, E., AND KARBASSI, H., "The Photolysis of Compressed Nitrous Oxide," *Helv. Chem. Acta.* 28, 1204 (1945).

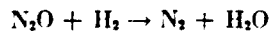
This paper is a study of the decomposition of nitrous oxide by the action of ultraviolet light (Hg-vapor lamp). At  $30^{\circ}\text{C}$  the decomposition of nitrous oxide is according to the following reaction:



By employing suitable filters it was found that only radiations of  $\lambda < 2200 \text{ \AA}$  are active. Reference is made to the previous study on the photochemical decomposition of nitrous and nitric oxides by Macdonald (*J. Chem. Soc.*, pp. 1-14 (1928)) who employed wavelengths 1860 to 1990  $\text{\AA}$ .

JOSHI, S. S., AND DESHMUKH, G. S., "Interaction of Nitrous Oxide and Hydrogen in the Silent Discharge," *Nature* 155, 483 (1945).

This is a study of the effects of pressure, applied potential, and the  $\text{N}_2\text{O}:\text{H}_2$  ratio on the following reaction.



The authors state that marked traces of ozone are observed in the decomposition of nitrous oxide by silent discharge. Oxygen and water vapor were also observed.

## 1916

ADEL, ARTHUR, "A Possible Source of Atmospheric  $N_2O$ ," *Astron. J.* 52, 40 (1946).

In the present paper Adel refers to the existence of nitrous oxide in the earth's atmosphere. This was established by the author (1939 and 1941) by the observation of the absorption band at  $7.77 \mu$  in the solar spectrum.

The origin of nitrous oxide in the atmosphere at the time of the paper (1946) is still in doubt. Its presence in the upper atmosphere is not readily explained by the photochemistry of the air.

Reference is made to the discovery by Kriegel (*Geophys.* 9, 447 (1944)) in which he suggested the slow decomposition of commercial fertilizers as a possible source of atmospheric nitrous oxide. Also the decay of vegetation under aerobic conditions was found by Kriegel to yield a gas with properties very similar to nitrous oxide.

Adel raises the question that if it is indeed true that soil air contains nitrous oxide, soil air might be one source and perhaps the principal one of the atmospheric nitrous oxide layer.

ADEL, ARTHUR, "A Possible Source of Atmospheric  $N_2O$ ," *Science* 103, 280 (1946).

In a letter to the editor Adel refers to his own discovery (1939 and 1941) of the existence of nitrous oxide in the earth's atmosphere. This was established by the discovery and analysis on an absorption band at  $7.77 \mu$  in the solar spectrum.

The author calls attention to the examinations of soil air by Kriegel (*Geophys.* 9, 447 (1944)). Kriegel called attention to the fact that elemental nitrogen in the form of ammonium salts, nitrites and nitrates is present in fertile soils. Also that one method for the preparation of pure nitrous oxide was by the decomposition of  $NH_4NO_3$  (ammonium nitrate) in accordance to the following reaction:



The probability that nitrous oxide in soil air might result from the slow decomposition of commercial fertilizers, and also by the decomposition of vegetation under aerobic conditions were considered by Kriegel. If this is true Adel suggests that soil air might be one source if not the principal source of the nitrous oxide layer in the upper atmosphere.

## 1917

ADEL, ARTHUR, "Atmospheric Temperatures from Infrared Emission Spectra of the Moon and Earth.

I. The Ozone Layer," *Phys. Rev.* 71, 564 (1947).

In this letter to the editor the author states that a fundamental and independent method of determining the temperature of the ozone layer has been applied to published infrared emission spectra of the moon, the earth, and the atmosphere (*Astrophys. J.* 103, 49 (1946)).

It is stated that the method is a general one, and is applicable equally as well to the  $H_2O$ ,  $N_2O$  and  $CO_2$  constituents of the atmosphere.

The temperature of the ozone layer was found to be  $-41^\circ C$  ( $229^\circ K$ ) for the evening of 5 September 1941, and  $-53^\circ C$  ( $220^\circ K$ ) for 3 November 1941.

PANDE, A., "Critical Survey of Recent Theoretical Work on the Ionosphere," *Terrestr. Mag. Atmos. Elec.* 52, 375 (1947).

This is an excellent survey of theoretical work on the ionosphere. A section on the composition and temperature of the upper atmosphere is given. The composition of the atmosphere at heights from 100 km to 167 km is discussed. Temperature at heights up to 250 km are given.

The author states that the latest theoretical and practical results have shown the presence of molecular nitrogen, molecular oxygen, atomic oxygen, water vapor and ozone. Reference is made to the literature establishing the presence of these constituents.

An extensive bibliography of 118 references is included.

SCHMALEISS, HANS, MANGTIERS, GERHARD, GODESCHEIT, MARGOT, AND SCHRAMM, HILDEGARD, "Detection of Traces of Nitrous Oxide. Application to prove Nonformation of Nitrous Oxide in Air Irradiated by Ultraviolet Light," *Z. anorg. Chem.* 253, 297 (1947).

In this paper the authors describe their method for the analysis of nitrous oxide. The gas sample is passed through potassium pyrogallol to remove oxygen. It is then passed over glowing platinum to decompose any nitrous oxide. The oxygen produced is detected colorimetrically with pyrogallate test paper. The sensitivity is 0.025 per cent by volume of  $N_2O$ . The method may be made more sensitive by concentrating the  $N_2O$  by freezing out below  $-102^\circ C$ .

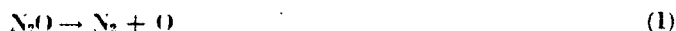
No trace of  $N_2O$  was obtained by passing air over a quartz mercury lamp. This is in direct contradiction to the claims of Kestner (*Klin. Wochschr.* 2, 1875 (1923)).

WHITTINGHAM, G., "Luminescent Decomposition of Nitrous Oxide," *Nature* 159, 232 (1947).

The purpose of the work described in this paper is to report observations on the nature of the luminescence accompanying the decomposition of nitrous oxide at temperatures around  $900^\circ C$ . A flow method was employed in the experiment. Nitrous oxide was passed continuously through an electrically heated quartz tube  $3 \times 20$  cm. A quartz window was at one end of the tube.

The spectrum was recorded with a Hilger medium quartz spectrocope. A continuum extending from the visible to the ultraviolet with a maximum intensity in the yellow-green was found. With long exposures weak emission bands superimposed on the continuum were observed and found to be due to nitrogen peroxide.

The primary dissociation is in accordance with the following reaction:



The formation of nitric oxide from the decomposition of nitrous oxide is considered to be due to the reaction of atomic oxygen with nitrous oxide.



At temperatures of from  $900^\circ C$  to  $1000^\circ C$  there is the possibility of the following primary dissociation.



1948

MIGEOTTE, MARCEL V., "New Identifications in the Infrared Solar Spectrum," *Astron. J.* 54, 45 (1949).

Using a new prism-grating spectrograph which was constructed in the laboratory of Dr. H. H. Nielsen

at the Ohio State University, Migeotte mapped and recorded the spectral regions from  $2.8 \mu$  to  $5.1 \mu$  and from  $7 \mu$  to  $11.7 \mu$ . The grating had rulings of 7200 and 3600 lines per inch respectively.

The new solar spectrograms showed bands of  $N_2O$  at  $3.9 \mu$ ,  $4.5 \mu$  and  $8.6 \mu$ . These observations may be taken as confirming the work of Adel and of Sutherland who previously had identified these bands in the solar spectrum. The present work may be considered as definite proof of the existence of atmospheric  $N_2O$ .

SHAW, J. H., SUTHERLAND, G. B. B. M., AND WORMELL, T. W., "Nitrous Oxide in the Earth's Atmosphere," *Phys. Rev.* 74, 978 (1948).

A series of solar spectra in the infrared region from  $2.5 \mu$  to  $5.0 \mu$  was observed at the Solar Physics Observatory, Cambridge, England. The authors employed a spectrometer with a lithium fluoride prism and a Hilger-Schwartz thermocouple as detector. The evidence of the presence of nitrous oxide in the atmosphere above the Observatory was established. Bands at  $3.90 \mu$ ,  $4.06 \mu$ , and  $4.50 \mu$  in the solar spectrum agree in wavelength with known absorptions of nitrous oxide. They agree in position, in relative intensity, and with bands obtained in the laboratory using an absorption cell filled with nitrous oxide with a Nernst filament as light source.

The  $4.5 \mu$   $N_2O$  doublet is a very intense band but is partially masked by the  $CO_2$  band at  $4.3 \mu$ . The authors were unable to establish the bands at  $7.8 \mu$  and  $8.6 \mu$  on which Adel (1939) based his first announcement of atmospheric nitrous oxide. The region about  $7.8 \mu$  is masked by the edge of the great  $6.3 \mu$  water vapor band when the observation is made at a low altitude station.

The authors conclude that their present work may be considered to confirm that of Adel in the identification of nitrous oxide in the atmosphere. The amount present in England is 1.0 atmo-cm which is of the same order as in America. It is suggested that it is reasonably certain that the presence of nitrous oxide in the upper atmosphere is a world-wide phenomenon. Its vertical distribution should be determined. It may be important in the atmosphere's radiative equilibrium if the maximum concentration occurs in the upper atmosphere.

TAYLOR, R. C., BROWN, R. A., YOUNG, W. S., AND HEADINGTON, C. E., "The Mass Spectrometer in Organic Chemical Analysis," *Anal. Chem.* 20, 396 (1948).

The utility of the mass spectrometer in the analysis of a number of gaseous mixtures is pointed out. The analysis of gas samples as small as  $10^{-4}$  ml is discussed. The relative intensity of principal peaks in mass spectra of some oxygenated compounds is given in Table 1 of the paper. The following values are given for  $N_2O$ .

m/e	Nitrous Oxide
14	13.8
16	6.24
28	13.8
29	0.28
30	35.9
31	0.22
44	100.0
45	0.73
46	0.22
Sensitivity of 100% peak (div./micron)	13.6
Sensitivity of n-butane at m/e 58	4.08

1949

ADEL, ARTHUR, "Atmospheric Nitrous Oxide," *Astron. J.* 54, 123 (1949).

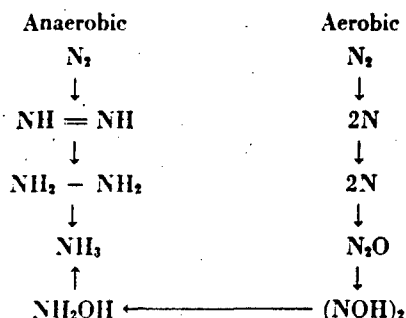
This is a brief note reporting that the observations of the absorption and emission of atmospheric nitrous oxide are being analyzed for the temperature of the gas. The note acknowledges the confirmation of the author's (1939-41) discovery of atmospheric nitrous oxides by Sutherland and his co-workers at Cambridge University, England.

Adel also calls attention to his suggestion (1946) that nitrous oxide escaping from soil air might constitute a possible source of nitrous oxide in the upper atmosphere.

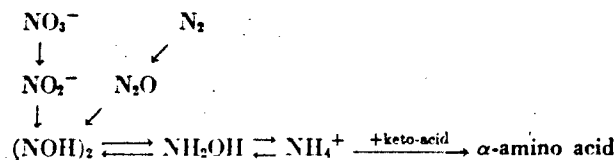
CLEMO, G. R., AND SWAN, G. A., "The Nitrogen Cycle in Nature," *Nature* 164, 811 (1949).

On 2 September 1949 at a Meeting of the British Association in Newcastle Section B (Chemistry) a discussion was held on "The Nitrogen Cycle in Nature." Professor A. I. Virtanen gave an account of the work which he had been carrying out at Helsinki in collaboration with other investigators.

Anaerobic nitrogen fixation proceeds most likely via reduction. In aerobic nitrogen fixation a primary oxidation of nitrogen is postulated. The two schemes are illustrated as follows:



The authors state that these two different routes while not attractive, at present, seem unavoidable. All the results obtained so far imply that all nitrogen sources produce chiefly ammonium nitrate prior to amino-acid synthesis.



MCMATH, ROBERT R., "Earth's Atmosphere," *Astron. J.* 54, 214 (1949).

This is a brief report on the research work at the McMath-Hulbert Observatory. Mention is made of the study of the line intensities in the near infrared telluric bands of  $N_2O$ .

A preliminary analysis of the  $2.13 \mu$  band of  $N_2O$  yields a value of 4 mm at N. T. P. for the abundance of atmospheric  $N_2O$ .

High-resolution studies of  $N_2O$  bands from  $2 \mu$  to  $3.6 \mu$  have been investigated.

MCMATH, ROBERT R., AND GOLDBERG, LEO, "Recent Exploration of the Infrared Solar Spectrum at the McMath-Hulbert Observatory," *Proc. Am. Philos. Soc.* 93, 363 (1949).

An account is given of the infrared solar spectrum with high resolution from  $1.4 \mu$  to  $3.6 \mu$ . Broad areas of the solar spectrum are completely masked by absorption in the earth's atmosphere. However, three relatively transparent "windows" centered approximately at  $1.6 \mu$ ,  $2.2 \mu$  and  $3.3 \mu$  permitted the recording of many hundreds of previously unobserved absorption lines. A detailed description is given of the McGregor tower telescope and spectrometer.

In the region  $2.9 \mu$  to  $3.6 \mu$  a band of  $N_2O$  appears at  $2.97 \mu$ . The authors state that to date (1949) the exploration of the infrared solar spectrum has disclosed new bands of methane ( $CH_4$ ), nitrous oxide ( $N_2O$ ), and the two isotopic forms of carbon dioxide  $C^{13}O_2^{16}$  and  $C^{12}O^{16}O^{18}$ .

Figure 5 in the paper shows a section of the  $2.13 \mu$  band of nitrous oxide in the solar spectrum as compared with the same series of lines from a laboratory experiment by the equivalent of 76 mm of  $N_2O$  at 1-10 atmospheric pressure. By comparing the two sets of intensities an equivalent atmospheric abundance for  $N_2O$  was found to be about 4 mm at atmospheric pressure and temperature of  $20^\circ C$ , or about one part in two million of the volume of the atmosphere.

$$1.0 \text{ 2,000,000} = 5 \times 10^{-6} \text{ percent by volume.}$$

A similar procedure for methane gave an atmospheric abundance of about 12 atmo-mm. The  $2 \mu$  region of the solar spectrum also showed other new bands. Two of these at  $2.13 \mu$  and  $2.26 \mu$  are due to nitrous oxide ( $N_2O$ ).

MELTZER, ROBERT J., ESTEY, ROGER, AND STRONG, JOHN, "Progress Report on High Altitude Infrared Transmission of the Atmosphere," O N R Contract N5ori-166, Task Order V, Johns Hopkins University, 10 January 1949.

This is a preliminary report of records obtained during the B-29 flights to 36,000 ft. (11 km). The Johns Hopkins infrared double monochromator was used in the flights to obtain infrared spectra of the sun. A description of the double monochromator is given.

Figure 7 of the report contains bands which have not been discussed and whose absorption vs altitude are not drawn. Reference is made to Hettner, Pohlmann, and Schumacher (*Z. Physik* 91, 372 (1934)) who attributed the bands in regions (I) and (II) Figure 7 to  $N_2O_5$ .

MOHLER, ORREN, AND PIERCE, A. KEITH, "An Improved Tracing of the Solar Spectrum between 2.9 and 3.6 microns," *Publ. Astron. Soc., Pacific*, 61, 221 (1949).

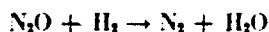
In this note from the McMath-Hulbert Observatory of the University of Michigan the authors have described their observations of the infrared solar spectrum using the McGregor spectrometer of the McMath-Hulbert Observatory. The region of investigation was extended to include  $2.9 \mu$  to  $3.6 \mu$ . This was made possible by the use of a refrigerated PbS cell.

In Figure 1 of the paper the solar spectrum is shown for the region from  $3.1 \mu$  to  $3.5 \mu$ . This was recorded with the new recorder. The figure does not show the region between  $2.9 \mu$  and  $3.1 \mu$ . The authors state that this region is dominated by the edges of the two water bands  $\nu_2$  centered at  $\lambda$  26,625 and  $\nu_1$  at 27,384. Near  $\lambda$  30,000 numerous individual lines belonging to the 00.0-02.1 band of  $N_2O$  are reported in the paper.

MORRIS, KELSO B., AND DAVIDSON, ETHEL M., "Determination of Nitrous Oxide," *Anal. Chem.* 21, 757 (1949).

This is a report of the determination of nitrous oxide in the products of certain oxidation studies under an Office of Naval Research contract.

There are two well-known methods, (a) slow combustion, and (b) catalytic reduction for determining and obtaining data on nitrous oxide and nitrous oxide-nitrogen methods. The following chemical equation represents the reaction in both methods:



The total contraction is equal to the volume of nitrous oxide.

Reference is made to Kobe and MacDonald (*Ind. Eng. Chem. Anal. Ed.* 13, 457 (1941)) who employed a silica gel catalyst containing 0.125 per cent of platinum. The nitrous oxide was reduced over the catalysts at 515° C by a limited excess of hydrogen.

The authors used a special Burrell Build-up gas analysis unit manufactured by the Burrell Technical Supply Company, Pittsburgh, Pennsylvania. The procedure and results of both methods are discussed.

NICOLET, M., "The Problem of the Ionosphere Region," *J. Geophys. Research* 54, 373 (1949).

The effects of the ultraviolet radiation from the sun on O<sub>2</sub>, O<sub>3</sub>, Na, H<sub>2</sub>O-vapor, N<sub>2</sub>, N<sub>2</sub>O, and He are described.

ROMAND, JACQUES, AND MAYENCE, JANINE, "The Absorption Spectrum of Nitrous Oxide in the Schumann Region," *Compt. rend.* 228, 998 (1949).

This is a report of an investigation of the absorption spectrum of N<sub>2</sub>O in the Schumann region. The spectral region studied was from 2150 Å to 1394 Å at 18°C and at pressures from 7.5 to 525 mm Hg. Absorption was found to be independent of the pressure within these pressures. Absorption maxima were observed at λ 1840 Å and λ 1450 Å. There was no evidence of photochemical dissociation ( $\text{N}_2\text{O} + h\nu \rightarrow \text{NO} + \text{N}$ ) even after long irradiation.

#### 1950

ADEL, ARTHUR, "Temperature of the Atmospheric Nitrous Oxide Layer," *Astron. J.* 55, 69 (1950).

The emissivity and radiation intensity of the atmospheric nitrous oxide layer was measured at 7.8 μ. The effective radiation temperature ranging from 0° and 10°C were found.

This evidence taken with the distribution of rotational intensities displayed by the atmospheric nitrous oxide bands suggest that the N<sub>2</sub>O layer is largely present in the troposphere.

ADEL, ARTHUR, "The Emission Spectra of the Earth's Surface, the Troposphere, and the Lower Stratosphere," *Centen. Proc. Roy. Meteorol. Soc.*, pp. 5-8 (1950).

The following table of polyatomic constituents of the earth's atmosphere is given. Their abundance is comparatively minute but important:



Compound	Amount
Water vapor ( $\text{H}_2\text{O}$ )	From $\frac{1}{4}$ mm to more than 50 mm liquid water layer equivalent
Carbon Dioxide ( $\text{CO}_2$ )	3 m N. T. P.
Ozone ( $\text{O}_3$ )	3 mm N. T. P.
Nitrous Oxide ( $\text{N}_2\text{O}$ )	5 mm N. T. P.
Methane ( $\text{CH}_4$ )	1 cm N. T. P.
Heavy water ( $\text{HDO}$ )	$10^{-4}$ of water vapor

Effective radiation temperatures of the atmosphere may be deduced from observations described in the paper, provided there is available also a solar or lunar spectrum showing in absorption the bands previously recorded in emission. In the temperature reduction of the data it is assumed that the molecule is present in an isothermal layer. This is stated to be largely an unknown value for nitrous oxide.

Assuming an isothermal layer one may take the emissivity of nitrous oxide at a particular wavelength to be equal to the absorptivity as given by the absorption spectrum. The method for calculating the radiation temperatures of  $\text{N}_2\text{O}$  and  $\text{O}_3$  is given.

The effective radiation temperature for nitrous oxide was found to lie between  $0^\circ\text{C}$  and  $10^\circ\text{C}$  in contrast to about  $-40^\circ\text{C}$ , the low ozonosphere temperatures. This temperature range for  $\text{N}_2\text{O}$  coupled with the well developed distribution of rotational intensities in the atmospheric absorption bands indicates that the nitrous oxide most likely resides in the troposphere.

BATES, D. R., AND NICOLET, M., "Oxides of Nitrogen," *J. Geophys. Research* 55, 306 (1950).

This paper is a study of the photochemistry of atmospheric water vapor. In the section of absorption cross-sections the different atmospheric gases are considered separately. With reference to the oxides of nitrogen the authors state that while the amount is unknown, nitric oxide ( $\text{NO}$ ) is present in the atmosphere since it is a dissociation product of nitrous oxide ( $\text{N}_2\text{O}$ ).

Nitrous oxide is stated to be certainly one of the constituents of the atmosphere. It is probably more abundant than ozone. Nitrous oxide has an ionization continuum beginning at about 1300 Å where  $\text{O}_3$  is transparent. No determination of the associated cross-section was made.

While absorption cross-sections for  $\text{N}_2\text{O}$  are not known with precision, laboratory measurements suggest the following values:

$$\begin{aligned}\text{At } 2900 \text{ Å, } & 5 \times 10^{-22} \text{ cm}^2 \\ \text{At } 1900 \text{ Å, } & 5 \times 10^{-19} \text{ cm}^2 \\ \text{At } 1450 \text{ Å, } & 1 \times 10^{-17} \text{ cm}^2\end{aligned}$$

There is lack of data on the vertical distribution of  $\text{N}_2\text{O}$ . It is probably confined mainly to comparatively low altitudes.

BENESCH, W., STRONG, JOHN, AND BENEDICT, W. S., "Progress Report on The Solar Spectrum from 3.3  $\mu$  to 4.2  $\mu$ ," O N R Contract 5Nori-166, Task Order V, Johns Hopkins University, 1 August 1950.

A prism-grating spectrograph with a cooled lead telluride detector was employed in obtaining the solar spectrum in the region 3.3  $\mu$  to 4.2  $\mu$ .

In the region  $2000-2400\text{ cm}^{-1}$  a few lines due to  $\text{H}_2\text{O}$  and  $\text{CH}_4$  were found. However, the principal feature is a well-defined band of  $\text{N}_2\text{O}$  whose center is at  $2564\text{ cm}^{-1}$ . Some 70 lines are distinguishable in this band. The next band of  $\text{N}_2\text{O}$  at  $2461.5\text{ cm}^{-1}$  did not appear as prominent because of the fall-off in the efficiency by the equipment at these longer wavelengths.

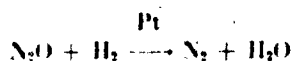
The several band features in this region of  $\text{H}_2\text{O}$ ,  $\text{HDO}$ ,  $\text{CH}_4$  and  $\text{N}_2\text{O}$  are discussed. With reference to  $\text{N}_2\text{O}$ , the  $2\nu_1$  band at  $2564\text{ cm}^{-1}$  is clearly resolved. The P-branch may be followed to  $J'' = 42$ , while the R-branch is not resolved above  $J'' = 31$ .

The authors refer to a Progress Report on absorption spectrum of the lower atmosphere from  $2.5\text{ }\mu$  to  $4.0\text{ }\mu$ , dated 15 September 1950, Johns Hopkins University. During these investigations a 60-inch army carbon arc searchlight was used as the infrared source. Horizontal path lengths of about 100 ft. to 900 ft. across the Johns Hopkins campus were employed in these studies. Absorption due to  $\text{N}_2\text{O}$  was not detected during these investigations.

BURKE, C. S., "Microdetermination of Nitrous Oxide in Gaseous Mixtures," *Mikrochimie ver. Mikrachim. Acta* 35, 135-159 (1950).

A survey is given of the reports of various workers, difficulties in the use of capillary burets, and the specific problems encountered in the analysis of very small samples of anesthetic gases which contain nitrous oxide. The present paper describes in detail the construction and operation of a special buret. The instrumental reading error in measurement is of the order of  $0.05\text{ }\lambda$ . One decimal fraction of 0.1000 inch is equivalent to  $45.5\text{ }\lambda$ . It is possible to measure  $200\text{ }\lambda$  with an accuracy of 1:2000.

The method involved is the reduction of the nitrous oxide in an excess of purified hydrogen at the surface of a hot platinum wire. The water thus produced by the reaction is absorbed by a drying agent, the change in volume represents directly the volume of nitrous oxide.



GOLDBERG, LEO, "Recent Advances in Infrared Solar Spectroscopy," *Reports Prog. Phys.* 13, 24 (1950).

The presence of nitrous oxide in the earth's atmosphere was first observed from spectroscopic evidence of the  $\nu_1$  fundamental at  $7.8\text{ }\mu$  by Adel (1939). Later the presence of atmospheric  $\text{N}_2\text{O}$  was confirmed by observation of additional bands at  $3.9\text{ }\mu$ ,  $4.5\text{ }\mu$  and  $8.6\text{ }\mu$  by Migeotte (1949); and by Shaw, Sutherland and Wormell (1948) through recognition of bands at  $3.9\text{ }\mu$ ,  $4.1\text{ }\mu$  and  $4.5\text{ }\mu$ .

Four additional bands of  $\text{N}_2\text{O}$  in the solar spectrum between  $2.0$  and  $3.0\text{ }\mu$  were found by McMath and Goldberg (1949) at the McMath-Hulbert and Mount Wilson Observatories. From laboratory experiments Plyler and Barker (1931) had previously observed three of the latter bands,  $2\nu_1 + \nu_1$  at  $3.0\text{ }\mu$ . The fourth band is extremely weak and is located at  $2.16\text{ }\mu$ . It was observed on a tracing obtained with the sun just above the horizon at the Mount Wilson Observatory. The identification of this fourth band was established with a high resolution tracing using an absorption cell containing  $25\text{ cm}$  of  $\text{N}_2\text{O}$  at atmospheric pressure.

The abundance of atmospheric  $\text{N}_2\text{O}$  was determined by McMath and Goldberg (1949) by comparing the intensities of the lines of the  $2.13\text{ }\mu$  band in the solar spectrum with that produced by a known amount

of  $\text{N}_2\text{O}$  in the laboratory. The telluric absorption was found to be equivalent to that which would be produced by 4 mm of  $\text{N}_2\text{O}$  at N. T. P.

HENZBERG, GERHARD, AND HERZBERG, L., "Rotation-Vibration Spectra of Diatomic and Simple Polyatomic Molecules with Long Absorbing Paths. VI. The Spectrum of Nitrous Oxide ( $\text{N}_2\text{O}$ ) below  $1.2 \mu$ ," *J. Chem. Phys.* 18, 1551 (1950).

This is a detailed report of the photographic infrared absorption spectrum of  $\text{N}_2\text{O}$  from laboratory studies. Long absorbing path lengths were used up to 4500 m atmos. The vibrational and rotational analyses are given.

McMATH, ROBERT R., PIERCE, A. KEITH, MOHLER, ORREN C., GOLDBERG, LEO, AND DONOVAN, RUSSEL A., "N<sub>2</sub>O Bands in the Solar Spectrum," *Phys. Rev.* 78, 65 (1950).

Credit is given to Adel (1939) for first detecting nitrous oxide in the earth's atmosphere through observations of the  $\nu_1$  fundamental at  $7.8 \mu$ . Observations of other  $\text{N}_2\text{O}$  bands at  $3.9 \mu$ ,  $4.1 \mu$  and  $8.6 \mu$  were subsequently made by Migeotte (1949) and by Shaw, Sutherland and Wormell (1948).

It is stated that the laboratory observation of Plyler and Barker (1931) suggested additional weaker bands of  $\text{N}_2\text{O}$  might appear in the solar spectrum. The bands predicted at  $2 \nu_2 + \nu_3$  at  $2.97 \mu$ ,  $2 \nu_1$  at  $2.26 \mu$ , and  $2 \nu_1 + \nu_3$  at  $2.13 \mu$  have all been found in the solar spectrum.

Comparison of telluric and laboratory intensities indicates the abundance of  $\text{N}_2\text{O}$  in the earth's atmosphere to be equivalent to that in a layer 4 mm thick at N. T. P.

MIGEOTTE, MARCEL V., "Fine Structure of  $\text{N}_2\text{O}$  Bands in the Infrared Solar Spectrum," *Astrophys. J.* 112, 136 (1950).

An excellent summary of the work on the presence of  $\text{N}_2\text{O}$  in the earth's atmosphere is given. The following table summarizes this review:

Observer	Date	Reference	Observation
Adel	1938	<i>Astrophys. J.</i> 88, 186 (1938); <i>ibid.</i> 90, 627 (1939).	Announced presence of $\text{N}_2\text{O}$ in earth's atmosphere to explain the band at $7.6 \mu$ region of prismatic solar spectrum.
Adel	1939	<i>Astrophys. J.</i> 90, 627 (1939).	Observed additional band $8.6 \mu$ attributed to $\text{N}_2\text{O}$ .
Adel	1941	<i>Astrophys. J.</i> 93, 509 (1941).	Identified individual rotational lines of $\text{N}_2\text{O}$ in atmospheric spectrum at $7.7 \mu$ .
Sutherland and Callendar	1943	<i>Reports Prog. Phys.</i> 9, 18 (1943).	Evidence for presence of $\text{N}_2\text{O}$ , while strong, was not entirely conclusive.
Adel	1941	<i>Astrophys. J.</i> 94, 451 (1941).	High resolution solar spectrograms did not show fine structure of $\text{N}_2\text{O}$ band at $8.6 \mu$ .
Migeotte	1948	<i>Astron. J.</i> 54, 45 (1948).	Stated that presence of atmospheric $\text{N}_2\text{O}$ was confirmed. Fine structure of $\text{N}_2\text{O}$ bands at $8.6$ , $4.5$ and $3.9 \mu$ shown.
Shaw, Sutherland	1948	<i>Phys. Rev.</i> 74, 978 (1948).	Independently found bands of $\text{N}_2\text{O}$ at $4.5$ , $4.06$ and $3.9 \mu$ on solar spectrum, lithium fluoride prism.
McMath	1949	<i>Astron. J.</i> 54, 214 (1949).	Fine structure due to $\text{N}_2\text{O}$ between $2$ and $3.6 \mu$ .

In the present paper by Migotte the results of observations made in the 8.6 and 4.5  $\mu$  regions of the solar spectrum are given. The prism-grating spectrograph employed in the study is described.

Figure 1 in the paper gives the fine structure of the solar spectrum obtained between 8.56  $\mu$  and 8.84  $\mu$ . Figure 2 shows the solar spectrum between 4.46  $\mu$  and 4.59  $\mu$ . Corresponding tables of wavelengths in these regions are included.

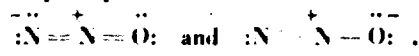
RICHARDSON, W. S., AND WILSON, E. BRIGHT, "The Infrared Spectrum of  $N^3N^{14}O$  and the Force Constants of Nitrous Oxide," *J. Chem. Phys.* 18, 694 (1950).

The investigation of the infrared spectrum of an isotopic modification of the molecule,  $N^3N^{14}O$ , of nitrous oxide is reported. The study provided a means of obtaining an additional datum from which the interaction constant  $f_{12}$  in the potential function

$$2V = f_1\Delta r_1^2 + f_2\Delta r_2^2 + 2f_{12}\Delta r_1\Delta r_2$$

could be determined. The observed frequencies were used in computing the force constant values,  $f_1 = 17.88$ ,  $f_2 = 11.39$ , and  $f_{12} = 1.36 \times 10^9$  dynes/cm, respectively.

These values are consistent with the electronic configuration of  $N_2O$  that the structure is a resonance hybrid resonating between the two (principal) structures,



SHAW, J. H., ONHOUM, M. L., AND CHAPMAN, R. M., "Fine Structure of  $N_2O$  near 4.06  $\mu$  in the Solar Spectrum," *Phys. Rev.* 78, 497 (1950).

In a letter to the editor the authors announce their investigations of the solar spectrum in the region 3.0  $\mu$  to 4.2  $\mu$ . A prism-grating spectrometer of the Pfund type equipped with a 7200 line per inch echelette replica grating, and a Perkin-Elmer 13-cycle per second thermocouple-amplifier system was used.

The identification of the 4.06  $\mu$  band had previously been reported by Shaw, Sutherland and Wormell (*Phys. Rev.* 74, 978 (1948)). In the present work reported in this letter over 70 rotation lines in this 4.06  $\mu$  band were observed. The absorption of the strongest lines was not more than 10 percent.

SLOBOD, R. L., AND KROGH, M. E., "Nitrous Oxide as a Constituent of the Atmosphere," *J. Am. Chem. Soc.* 72, 1175 (1950).

In this paper the authors have isolated and as a result confirmed the presence of nitrous oxide as a constituent of the atmosphere. The nitrous oxide was separated from the more volatile gases in the atmosphere by a type of fractional distillation. After this separation the nitrous oxide was identified by the use of the mass spectrometer.

The results for ten samples of air from six locations including five from Texas and one from Wyoming are given in the report. The apparatus and method are described and discussed in detail. In the following table of the concentration of the more rare constituents in the atmosphere, nitrous oxide is included.

Constituent	Percent by Volume in Dry Air
Hydrogen	0.01
Neon	0.00123-0.0018
Helium	0.0004-0.0005
Krypton	0.00005-0.0001
Nitrous oxide	0.00005
Xenon	0.000006-0.000008

Nitrous oxide was found to be present to the extent of  $0.00005 \pm 0.00001$  percent by volume. The value 0.00005 percent by volume for the nitrous oxide content was based upon the results of the analysis of ten samples of air.

It is pointed out that from absorption data the amount of atmospheric nitrous oxide was estimated to be equivalent of a layer of gas several millimeters thick at N. T. P. It is interesting to note that a layer four millimeters thick corresponds to exactly the concentration of 0.00005 percent found by the authors in the present paper. A value obtained by Shaw, Sutherland and Wormell (*Phys. Rev.* 74, 978 (1948)) based on adsorption data from solar spectra is slightly in excess of that obtained by Slobod and Krogh.

Since the nitrous oxide was actually isolated from ground samples of air suggests that it is not present merely as a thin layer in the upper atmosphere but is distributed throughout the atmosphere.

WORMELL, T. W., "Nitrous Oxide in the Earth's Atmosphere," *Centen. Proc. Roy. Meteorol. Soc. (London)*, p. 30 (1950).

In the discussion which followed the symposium on Radiation and its Effect on the Troposphere and Lower Stratosphere, Wormell alludes to Adel's pioneer work in the infrared solar spectrum in establishing strong evidence for the existence of nitrous oxide in the earth's atmosphere. An investigation at Cambridge, England by Shaw, Sutherland and Wormell (reported in *Phys. Rev.* 74, 978 (1948)) showed that it was impossible working near sea level to observe either of the bands at  $7.8 \mu$  and  $8.6 \mu$  found by Adel.

The band at  $7.8 \mu$  was lost by the water band centered at  $6.3 \mu$ , while the  $8.6 \mu$  band (a weak band) was concealed by other structures in the spectrum. However, using a prism of lithium fluoride Shaw, Sutherland and Wormell were able to identify three shorter wavelength bands in the solar spectrum at  $3.9 \mu$ ,  $4.06 \mu$  and  $4.50 \mu$  attributed as being due to nitrous oxide. This established that nitrous oxide is a widespread and normal constituent of the atmosphere. The total amount of nitrous oxide in the atmosphere is of the same order as the total amount of ozone.

A report under the auspices of the Admiralty Atmospheric Transmission in the 1-14 micron region (A. R. L. R. 4 e 600 (1949)) indicated that radiation which traversed a horizontal path of two miles near sea level showed the nitrous oxide bands at  $3.9 \mu$  and  $4.5 \mu$  with considerable intensity. This observation confirmed Adel's conclusion from the estimate of mean temperature that most of the  $N_2O$ , unlike ozone, occurs in the lowest layers of the atmosphere.

1951

ADEL, ARTHUR, "Atmospheric Nitrous Oxide and the Nitrogen Cycle," *Science* 113, 624 (1951).

A brief review of Adel's discovery of nitrous oxide in the earth's atmosphere is given. The amount of nitrous oxide present is comparable with that of atmospheric ozone, about 3 mm N. T. P. Reference is made to the discovery of Krieger (1944) that nitrous oxide is one of the most abundant constituents of soil air, and to Adel's suggestion (1946) that escaping soil air might well be the principal source of atmospheric nitrous oxide.

The purpose of the present note is to summarize the several lines of evidence to support the early hypothesis of the origin of nitrous oxide, that its layer is "adjacent" to the earth's surface, and that atmospheric nitrous oxide is an important phase in the nitrogen.

(a) The effective radiation temperature of atmospheric nitrous oxide is about  $10^{\circ}\text{C}$ . This is deduced from observations of the atmosphere's infrared emission spectrum.

(b) A British Admiralty group found from infrared atmospheric transmission that large concentrations of nitrous oxide were present in air paths parallel and close to the surface of the land and sea.

(c) Solar spectra recorded aboard high-flying aircraft revealed a greatly diminished absorption by nitrous oxide in the  $7.8\ \mu$  region.

(d) A recent mass spectrographic analysis by Slobod and Krogh (*J. Am. Chem. Soc.* 72, 1175 (1950)) showed that the concentration of nitrous oxide in the atmosphere near ground level is about  $5 \times 10^{-4}$  percent by volume.

Adel concludes that it appears very likely that nitrous oxide escapes from the soil into the atmosphere, and that this escape constitutes an important phase of the nitrogen cycle. It is pointed out for the first time by Adel how nitrogen captured from the atmosphere and fixed in the soils of the earth is ultimately returned to the atmosphere at the end of the nitrogen cycle.

(a) Nitrous oxide appears in the soil as a decomposition product of the fixed nitrogen compounds.

(b) The nitrous oxide diffuses into the atmosphere.

(c) Nitrous oxide in the upper atmosphere is decomposed photochemically by  $\lambda < 2000\ \text{\AA}$  into  $\text{N}_2$ ,  $\text{O}_2$  and  $\text{NO}$ . At these high atmospheric levels  $\text{NO}$  is also decomposed photochemically into nitrogen and oxygen by  $\lambda < 2000\ \text{\AA}$ .

(d) It is concluded that presumably the nitrous oxide accumulates above the earth's surface until the rates of accumulation and decomposition are equal.

ADEL, ARTHUR, "Concerning the Vertical Distribution and Origin of Atmospheric Nitrous Oxide," *Astron. J.* 56, 33 (1951).

This brief note is an abstract of a paper presented by the author at the Eighty-fourth Meeting of the American Astronomical Society, Haverford, Pennsylvania 27-30 December 1950.

This paper is identical to Adel's note on Atmospheric Nitrous Oxide and the Nitrogen Cycle published in *Science* 113, 624 (1951). The abstract is given in full under the latter reference.

ADEL, ARTHUR, "Rotational Structure in the *R* Branch of the Atmospheric Nitrous Oxide Band at  $8.6\ \mu$ ," *Astrophys. J.* 113, 222 (1951).

In this note to the *Astrophysical Journal*, Adel calls attention to a recent discussion by Migeotte (*Astrophys. J.* 112, 136 (1950)) of the fine structure in the *R* Branch of the very weak nitrous oxide band at  $8.6\ \mu$  in the atmospheric spectrum.

Migeotte as well as Sutherland and Callendar (*Reports Prog. Phys.* 9, 18 (1943)) mistakenly assert that the faint fine structure of this weak and minor band is completely absent from Adel's grating map of the infrared solar spectrum published in *Astrophysical Journal* 94, 451 (1941).

Adel points out that figure 28 of the map unmistakably reveals ten lines in the *R* Branch of the weak  $8.6\ \mu$  band. These lines are listed in Table I of the present paper by Adel.

CALLOMON, H. J., MCKEAN, D. C., AND THOMPSON, H. W., "Intensities of Vibration Bands. III. Nitrous Oxide," *Proc. Roy. Soc., (London)* A 208, 332 (1951).

In this paper the laboratory results are given for the measurement of the absolute intensity of the vibration absorption band of nitrous oxide at  $4.5 \mu$ . The experimental method is described. There is a discussion of the results obtained, the correlation of intensity with polar intensities, and pressure-broadening relationships.

GEBBIE, H. A., HARDING, W. R., HILSUM, C., PRYCE, A. W., AND ROBERTS, V., "Atmospheric Transmission in the 1 to  $14 \mu$  Region," *Proc. Roy. Soc. (London)* A 206, 87 (1951).

The authors describe their observations and results on the transmission of the atmosphere for radiation of wavelengths in the spectral region  $1 \mu$  to  $14 \mu$ . These measurements were made at sea level. Absorption bands due to water vapor, carbon dioxide and the minor constituents of the atmosphere,  $N_2O$  and  $HDO$  were observed.

The apparatus used is described in detail as well as the experimental procedure and interpretation of records. The elevation was over paths up to 2.5 miles (4 km).

The  $N_2O$  band at  $4.5 \mu$  was observed. This corresponded with the fundamental  $\nu_3$  of nitrous oxide. Absorption at  $7.7 \mu$  and  $7.9 \mu$  in the spectrograms obtained by these investigators coincided with nitrous oxide bands. It is pointed out that these experiments show that nitrous oxide is present at sea level.

GOLDBERG, LEO, "The Analysis of the Solar and Terrestrial Atmospheres," *Proc. Am. Acad. Arts and Sci.* 79, 238 (1951).

High-resolution studies of the infrared solar spectrum until a few years ago was limited to about 14,000 Å. At this region of wavelength the sensitivity of the photographic plate becomes effectively zero. The development of the lead sulfide photocell has made it possible to extend high resolution studies of the spectrum to about 36,000 Å.

There are several reasons why spectroscopic studies of the solar and terrestrial atmospheres are important. Analysis of the intensities of lines provide important information of the earth's atmosphere. Among the constituents studied in this manner are  $CO_2$ ,  $CH_4$ ,  $N_2O$  and  $H_2O$  vapor. Such data as the abundance, the vertical distribution and the temperature gradient may be obtained. The abundance and vertical distribution may be determined with quite good accuracy.

The total quantity of methane in the earth's atmosphere has been estimated to be equivalent to that which would be contained in a layer 1.2 cm thick at N. T. P. The abundance of  $N_2O$  is about 4 atmo-mm. The distribution of methane in the earth's atmosphere appears to be world-wide in character. It has been observed at an altitude of 6000 feet at Mount Wilson Observatory. Its density falls off experimentally with height following the same rate as the main body of the atmosphere.

The author states that determinations of abundance and vertical distribution would provide information both on the origin of the rare constituents of the atmosphere such as  $CH_4$  and  $N_2O$  and also on the temperature balance of the atmosphere.

Ultraviolet radiation from the sun is absorbed by ozone in the earth's atmosphere and infrared radiation from the surface of the earth by ozone, water vapor and carbon dioxide. Also the atmosphere loses energy

by infrared emission of ozone, water vapor and carbon dioxide. If the abundance and vertical distribution along with the absorption coefficients these data should make it possible to calculate the atmospheric temperature gradient.

GOODY, R. M., AND ROBINSON, G. D., "Radiation in the Troposphere and Lower Stratosphere," *Quart. J. Roy. Meteorol. Soc.* 77, 151 (1951).

In this excellent review of modern meteorology the authors state by way of introduction that it is only through the absorption of solar radiation and the emission to space of low-temperature terrestrial radiation from the earth and atmosphere that our planet can receive and lose energy. These two radiative processes are the source and sink of the terrestrial heat energy which is our atmosphere.

The principal gaseous constituents of the atmosphere are transparent to their radiation. The minor constituents as  $H_2O$ -vapor,  $CO_2$ ,  $O_3$ ,  $N_2O$ , etc. have intense and complex absorption spectra. The absorption bands of these constituents in the solar spectrum have been most widely employed to detect and measure their distribution.

The integrated absorption is defined by the following relationship:

$$A_r(m) = \int_r A_r(m) d\nu = \text{integrated absorption} \quad (1)$$

where the integral embraces the  $r$ th absorption band. In this equation  $m$  is the amount of absorbing matter, where  $\rho$  is the density and

$$m = \int \rho dz \quad (2)$$

$z$  is the height above the earth's surface.  $\nu$  in (1) is the frequency. If the quantity of absorbing material is very small, the authors give the following expression

$$A_r = m \int_r k\nu d\nu \quad (3)$$

in which  $k\nu$  is the absorption coefficient. Goody and Wormell (*Proc. Roy. Soc. (London)* A 209, 178 (1951)) have shown that using the  $7.8 \mu$  and  $8.6 \mu$  bands of nitrous oxide that one can make a fairly precise determination. As a result it is possible to obtain information upon intensities required in atmospheric problems.

Equation (3) predicts that for small absorptions the integrated absorption varies linearly with the amount of absorbing material, and the slope in the band intensity.

GOODY, R. M., AND WORMELL, T. W., "The Quantitative Determination of Atmospheric Gases by Infrared Spectroscopic Methods. I. Laboratory Determination of the Absorption of the  $7.8 \mu$  and  $8.6 \mu$  Bands of Nitrous Oxide with Dry Air as a Foreign Gas," *Proc. Roy. Soc. (London)* A 209, 178 (1951).

The authors state that the aim of the present investigation was (1) to obtain information which would permit quantitative interpretation of nitrous oxide bands in solar spectra recorded at different levels in the atmosphere, (2) to be able to calculate the contribution of nitrous oxide to the thermal balance of the atmosphere, and (3) to test a technique which would be applicable to other atmospheric gases.

The investigation was carried out on the  $7.8 \mu$  band. Information was also obtained on the  $8.6 \mu$  band. The experimental method and instrumentation are given as well as the source of error. The measurements were quite complete, and the results are fully discussed.



The conclusion is that the method described in the present investigation can be applied to obtain all the information about the 7.8 and 8.6  $\mu$  bands of nitrous oxide which is required for quantitative identification of telluric spectra. This includes line intensities, the nature of line-broadening mechanisms, and the consequent line shape, the line widths and the effect of temperature and pressure upon them.

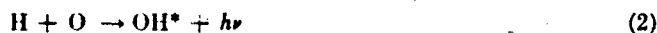
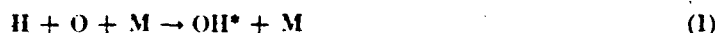
HERZBERG, G., "The Atmospheres of the Planets," *J. Roy. Astron. Soc. (Canada)* 45, 100 (1951).

In this paper which was read at the Symposium on "Atmospheres of the Stars and Planets" held by the Royal Society of Canada at Kingston June 1950, Herzberg gave a review of the present status of spectroscopic investigations of the earth and the terrestrial planets. Reference is made to the discovery of the presence of  $N_2O$  in the atmosphere of the earth by Adel (*Astrophys. J.* 90, 627 (1939); *ibid.* 93, 509 (1941); and *ibid.* 94, 451 (1941)) and by Shaw, Sutherland and Wotmell (*Phys. Rev.* 74, 978 (1948)).

KRASOVSKI, V. I., "On the Mechanism of the Illumination of the Night Sky," *Dokl. Akad. Nauk., SSSR* 77 (No. 3), 395 (1951).

In this paper Krasovski discusses critically the intensities of the OH lines given by Meinel (*Astrophys. J.* 111, 555 (1950)). Reference is made to the paper on the Theory of the Spectral Emission from the OH Molecule in the Night Sky Spectrum by Bates and Nicolet (*Compt. rend.* 230, 1943 (1950)). These investigators assumed a primary photo-dissociation of  $H_2O$  at altitudes up to 70 km by solar radiation. They developed a theory to explain the OH emission from the night sky.

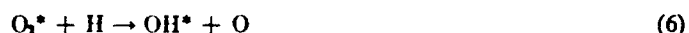
According to the theory of Bates and Nicolet the origin of the emission is from a layer at about 80 km, in which  $H_2O$ , OH,  $HO_2$  and H exist together in proportions determined by the height-concentrations of O and  $O_3$ . Three possible processes are given.



Between 60-80 km reaction (3) is considered to predominate. For an emitting layer of 10 km thickness at 80 km, the theory predicts an excitation level of  $5 \times 10^{10}$  quanta  $cm^{-2} sec^{-1}$ .

Krasovski states that the above theory of Bates and Nicolet, i.e. the hydrogen-oxygen mechanism for excitation of OH is not in accord with the results of Rodionov (*Izv. Akad. Nauk., SSSR, Ser. Fiz.* 14 (No. 3), 247 (1950)). Another hypothesis is proposed in the present paper.

It is assumed that  $N_2O$  is formed in large amounts as a result of a three body collision in the layer where dissociated oxygen exists. By diffusion the  $N_2O$  is vertically displaced to higher levels. The  $N_2O$  then reacts with atomic oxygen. The excited  $O_2$  molecules thus produced react with hydrogen atoms to give excited OH molecules.



KRASOVSKI, V. I., AND LUKASHENYA, V. T., "Identification of the Night Sky Spectrum in the 10,000 Å Region," *Dokl. Akad. Nauk., SSSR* 80, 735-738 (1951).

The authors in this paper discuss the night sky spectrum in the region of the 9700-10,300 Å bands. A spectrograph having a dispersion of about 175 Å mm and a resolving power to 5 Å was used in this study.

Bands in this spectral region previously considered to be due to OH may be due to NH. The primary excitation is thought to be due to ternary collisions giving rise to the formation of excited molecules of O<sub>2</sub>, NO, N<sub>2</sub>, O<sub>3</sub>, and N<sub>2</sub>O.

MURRAY, R. B., "The Near Infrared Spectrum of Nitrous Oxide with Long Absorbing Paths," *Phys. Rev.* 83, 486 (1951).

This is an abstract of a paper read before the Seventeenth Annual Meeting of the Southeastern Section of the American Physical Society held at the University of Chattanooga 5-7 April 1951.

A 22-meter multiple reflection absorption cell was employed. The infrared spectrum of nitrous oxide was observed with a prism spectrometer from 1.25 to 2.5 μ with a maximum path length of 554 atmometers.

SHAW, J. H., CHAPMAN, R. M., HOWARD, J. N., AND OXHOLM, M. L., "A Grating Map of the Solar Spectrum from 3.0 to 5.2 Microns," *Astrophys. J.* 113, 268 (1951).

This is a study of the infrared solar spectrum from 3.0 μ to 5.2 μ obtained at the Ohio State University with a high-resolution Pfund-type grating spectrometer.

Among the bands and lines identified are the following: N<sub>2</sub>O, HDO, CO<sub>2</sub>, CO, CH<sub>4</sub>, and N<sub>2</sub>O. With respect to the existence of nitrous oxide in the atmosphere the authors include a brief summary of the discovery and evidence for the existence of atmospheric nitrous oxide.

Values from 0.5 to 1.0 p.p.m. in the atmosphere have been suggested by various writers for the abundance of atmospheric nitrous oxide from comparison with laboratory spectra.

Three bands of N<sub>2</sub>O are shown in the grating map in the present paper. (a) The fundamental ν<sub>2</sub> at 4.5 μ, (b) the overtone 2 ν<sub>1</sub> at 3.9 μ, and (c) the weak combination band at 4.06 μ.

TAYLOR, J. H., "Two New Absorption Bands of N<sub>2</sub>O," *J. Chem. Phys.* 19, 1314 (1951).

This is a report on the observation of the 0 1 0 → 1 0 0 and 0 2 0 → 1 1 0 bands of the nitrous oxide molecule.

A Perkin-Elmer Model 12-C infrared spectrometer was employed with a one-meter absorption cell filled to one atmosphere pressure.

THOMPSON, H. W., AND WILLIAMS, R. L., "Vibration-Rotation Bands of Nitrous Oxide," *Proc. Roy. Soc. (London)* A 208, 326 (1951).

The infrared absorption of nitrous oxide gas was studied near 4.5 μ. This was a laboratory study. The 4.5 μ band was measured using a lead telluride detector in a grating spectrometer.

One reason for studying this band is its importance in the determination of nitrous oxide in the upper atmosphere in which measurements on the intensity are needed. The investigators were able to determine the wavelength of the absorption lines. The results of their experiments are given and discussed.

1952

ADEL, ARTHUR, "The Atmospheric Window, 16 to 24 Microns, and the Second Fundamental of Nitrous Oxide," *Phys. Rev.* 88, 128 (1952).

In this paper Adel reports his further investigation of the atmospheric window, 16 to 24 microns. The window is defined by complete absorption by carbon dioxide on the short wavelength side and by complete absorption by water vapor on the long wavelength side. The author states that virtually nothing new of importance has been found about this region of the atmospheric spectrum. It has been found that the amount of solar radiation reaching the earth's surface in this spectrum region increases sharply with diminishing amount of precipitable water vapor content of the atmosphere. The transparency has been estimated as exceeding about ten percent in the 16-22  $\mu$  on the driest days.

This spectral region (16-22  $\mu$ ) is subject to daily and seasonal change which is related to the incessant fluctuation of water vapor content. A further investigation of this spectral interval has indicated the presence of the second fundamental of nitrous oxide with center at 17  $\mu$ .

In figure 1 in the paper the infrared solar-telluric spectrum is shown. The P, Q and R branches of the atmospheric 17  $\mu$  nitrous oxide band is clearly indicated. This was obtained through one millimeter of precipitable water. With this discovery all three fundamentals of nitrous oxide have now been identified in the telluric spectrum:  $\nu_1$  at 7.8  $\mu$ ,  $\nu_2$  at 17.0  $\mu$  and  $\nu_3$  at 4.5  $\mu$ . Reference is made to the confirmation of the existence of the new window by Migeotte and Levin (*Astrophys. J.* 115, 326 (1952)), and by Anthony (*Phys. Rev.* 85, 674 (1952)).

ANTHONY, R., "Atmospheric Absorption of Solar Infrared Radiation," *Phys. Rev.* 85, 674 (1952).

In this letter to the editor the author reports his results of some measurements of solar radiation taken with a KBr double monochromator in the infrared spectral region 1.5 to 20 microns. From the data collected absorption coefficients for the continuous spectrum in the 8 to 20 spectral interval were evaluated.

With reference to the window in the region 17-20 microns found by Adel (*Astrophys. J.* 96, 239 (1942)) Anthony was able to confirm this. This spectral region is highly sensitive to water vapor content as found by Fowle (*Astrophys. J.* 42, 394 (1915)).

BATES, D. R., "Some Reactions Occurring in the Earth's Upper Atmosphere," *Ann. Geophys.* 8, 194 (1952).

This is a communication presented at the Assembly of the International Union of Geodesy and Geophysics, Brussels (1951). Reference is made to the infrared researches of Adel and other workers who found that nitrous oxide is an important atmospheric constituent and its molecular abundance is about  $2 \times 10^{19}/\text{cm}^2$  column.

Bates and Witherspoon (1952) employing absorption cross sections derived from several laboratory investigations of different groups of investigators have calculated the rate of photodissociation by



which begins at about  $\lambda$  3070 Å, and the reaction



that begins at  $\lambda$  2400 Å.

Two levels of nitrous oxide were considered (a) ground level, and (b) the 70 km level, and assuming that all the nitrous oxide is contained in a 10-km layer at one or the other of these levels. The calculations show that if the layer were at ground level the number of  $N_2O$  molecules destroyed by photodissociation would be some  $5 \times 10^4$   $cm^3$  sec. At the 70-km level the number would be some  $3 \times 10^7$   $cm^3$  sec.

These large destruction rates suggest that many of the sources of nitrous oxide heretofore advocated can be dismissed since the parent particles involved are not produced sufficiently rapidly. Bates and Witherspoon (1952) have shown that the only plausible parent particles are the O atoms and  $O_3$  molecules in the lower atmosphere by which equilibrium is preserved by the following reactions.



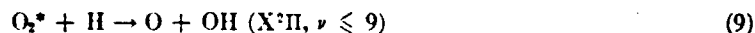
The author states that though photodissociation in the Herzberg continuum may proceed slowly in the troposphere, mixing and replenishment by reaction (1) might insure an ample supply of both O and  $O_3$ .

Nitrous oxide might result from the following reactions.



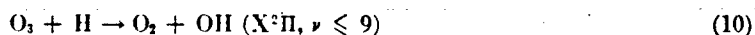
It is remarked that if one of these reactions were indeed the source that nitrous oxide would be prevalent in the troposphere as demanded by the determinations of Slobod and Krogh (1950).

With reference to Adel's (1951) suggestion that the action of soil microorganisms is responsible for atmospheric nitrous oxide, Bates refers to Hutchinson (*Am. Sci.* 32, 178 (1944)). Calculations indicate that Adel's hypothesis requires that nitrous oxide be a major end-product of denitrification. In the present paper Bates also has examined the hypothesis proposed by Krasovski (*Dokl. Akad. Nauk.* 77, 395 (1951)) that nitrous oxide is involved in the excitation of the Meinel hydroxyl bands in the excitation of the night airglow by the following reactions.



These reactions are considered to be unacceptable. Observations indicate that the OH bands have an intensity corresponding to a photon emission of about  $10^5$   $cm^3$  sec, and that they originate from a layer of altitude about 70 km. The concentration of  $N_2O$  at the 70-km level is considered to be quite small by Bates, and at this level photodissociation is rapid.

The process suggested by Henrique, Duncan and Noyes (*J. Chem. Phys.* 6, 518 (1938))



still seems attractive.

BATES, D. R., AND WITHERSPOON, AGNES E., "The Photochemistry of Some Minor Constituents of the Earth's Atmosphere," ( $CO_2$ , CO,  $CH_4$ ,  $N_2O$ ), *Mon. Not. Roy. Astron. Soc.* 112, 101 (1952).

In the following Table are compiled the current estimates of the particle concentrations,  $n(M)$ , and temperatures,  $T$ , at various altitudes,  $z$ , up to 130 kilometers.

Structure of the Atmosphere

Altitude $z$ (km)	Particle Concentration $n(M) \text{ cm}^{-3}$	Temperature $T$ deg. K
130	$1.2 \times 10^{11}$	450
120	$2.7 \times 10^{11}$	360
110	$7.4 \times 10^{11}$	305
100	$2.3 \times 10^{12}$	270
90	$8.7 \times 10^{12}$	245
80	$3.9 \times 10^{13}$	215
70	$2.5 \times 10^{14}$	190
60	$8.2 \times 10^{14}$	275
50	$2.3 \times 10^{15}$	290
40	$6.8 \times 10^{15}$	250
30	$3.9 \times 10^{17}$	225
20	$2.0 \times 10^{19}$	220
10	$8.8 \times 10^{19}$	220
0	$2.6 \times 10^{19}$	285

Reference is made to the first discovery of the presence of nitrous oxide in the atmosphere by Adel (1938, 1939, 1941) from his observations on the  $7.6 \mu$  region of the solar spectrum. Confirmatory evidence was afterwards obtained by other investigators working in the infrared. The abundance of nitrous oxide in the atmosphere has been estimated to be 0.8 atmo-cm or  $2 \times 10^{19}$  molecules  $\text{cm}^2$  column. With reference to the location the authors state that this has not been properly determined. If the nitrous oxide were mainly confined to a layer 10 km thick (the approximate scale height in the lower and middle atmosphere), the authors state that the mean concentration would be about  $2 \times 10^{13} \text{ cm}^{-3}$ . The total particle concentration at an altitude of 70 km is only  $2.5 \times 10^{14}$ . Therefore it would seem most unlikely that the nitrous oxide could be so high.

With reference to absorption of nitrous oxide it is stated that the long wavelengths limits of the continua are not well defined. However, it appears that a very weak absorption begins at  $\lambda 3070$ , and the main absorption begins at about  $\lambda 2400$ . The products of dissociation are not definitely known. In the low-energy region the following process most likely occurs.



In the region of high-energy there is considerable evidence for the following reaction.



The authors state that it is by no means obvious that there is any upper atmospheric reaction capable of yielding nitrous oxide necessary to maintain the observed abundance. The question as to whether the nitrous oxide could originate on, or near, the earth's surface is considered. The following processes are considered and thoroughly discussed.

(1) Formation of nitrous oxide by soil microorganisms.

(2) Homogeneous gas reactions.

(a) Bamford suggested the formation of  $\text{N}_2\text{O}$  from  $\text{O}^+$  ions in some unspecified way.

(b) (Nicolet)  $\text{O}^- + \text{N}_2 \rightarrow \text{N}_2\text{O} + \text{e}^- \quad (3)$

Both (a) and (b) are unacceptable for the rate of production of neither ion even approaches the necessary value.

(c) Metastable nitrogen molecules.



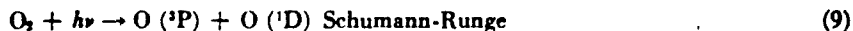
(d) Metastable oxygen molecules,  $O_2 (a' \Delta_g \text{ or } b' \Delta_g^+)$



(e)  $HO_2 + N_2 \rightarrow N_2O + OH \quad (8)$

The authors conclude that the main processes outlined above all fail, because the supply of the parent particles is inadequate to balance the loss that would be incurred in producing the nitrous oxide at as great a rate as it is being destroyed.

In the first part of the present paper the altitude distribution of the rate of photodissociation of molecular oxygen was calculated. It is shown to be characterized by two maxima one due to the Schumann-Runge continuum beginning at  $\lambda$  1759, and the other due to the Herzberg continuum beginning at  $\lambda$  2421. The altitudes are approximately 100 km and 30 km respectively.



The yield of oxygen atoms in (9) is about  $1 \times 10^7/\text{cm}^2/\text{sec}$ ; that in (10) about  $5 \times 10^7/\text{cm}^2/\text{sec}$ .

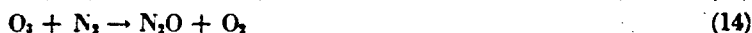
The region near 30 km is discussed. Here the atomic oxygen initially formed reacts rapidly to give ozone.



The ozone thus formed by photodissociation rapidly reliberates atomic oxygen.

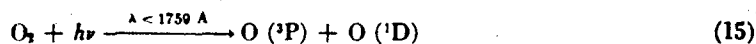


As a result the supply of either atomic oxygen or ozone is sufficient to meet the nitrous oxide requirement.



Processes (13) and (14) are discussed in detail with respect to requirements, rate coefficients, laboratory evidences, energies, and temperature. The argument seems to favor process (14) as most likely to meet all requirements.

Schumann-Runge continuum



Herzberg continuum



In the presence of a third body the atoms thus liberated may recombine,



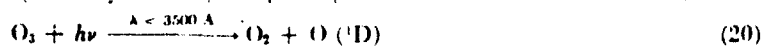
or they may unite with oxygen molecules forming ozone.



The ozone may be destroyed by the collision process



and by photodissociation in the strong Hartley continuum beginning at about  $\lambda$  3500 Å



and in the weak Chappuis continuum beginning at about 8000 Å.



MAYENCE, J., "Absorption Spectra at Low Temperature. Study of  $\text{N}_2\text{O}$  gas, and  $\text{NO}$  gas and liquid," *Ann. Phys. (Paris)* 7, 453-505 (1952).

It was found that at 18°C  $\text{N}_2\text{O}$  gas had absorption peaks at  $\lambda$  1840 Å and  $\lambda$  1450 Å. There was no evidence of photodissociation of nitrous oxide to nitric oxide for wavelengths down to 1390 Å.

MCMATH, ROBERT R., "Solar Research at the McMath-Hulbert Observatory," *Pub. Astron. Soc. (Pacific)* 64, 151 (1952).

In this general discussion of solar research the author states that terrestrial carbon dioxide, methane and nitrous oxide in the earth's atmosphere show remarkable intensity variations with changes in the altitude of the sun.

Nitrous oxide is almost absent in the noonday solar spectrum at wavelengths short of 2.5  $\mu$ . However, it becomes easily visible as the sun approaches the horizon. Studies of the vertical distribution are not completed.

MIGEOTTE, M. V., "On the Presence of Atmospheric Gases from Infrared Telluric Bands," *The Atmospheres of the Earth and Planets*, Edited by Gerald P. Kuiper, The University of Chicago Press, Chicago, Illinois (1952), p. 284.

A brief review of the following atmospheric gases is given:  $\text{O}_3$ ,  $\text{N}_2\text{O}$ ,  $\text{CH}_4$ ,  $\text{CO}$ ,  $\text{HDO}$ , and  $\text{NH}_3$ . With reference to nitrous oxide brief mention is made of the discovery of the presence of atmospheric nitrous oxide by Adel in 1939. Recent progress in infrared studies of the solar spectrum has been made at the McMath-Hulbert Observatory, the Mount Wilson Observatory, the Ohio State University, Johns Hopkins University, and the International Scientific Station of Jungfraujoch, Switzerland.

The Jungfraujoch Observatory has been used by M. V. Migeotte in collaboration with Dr. L. Neven of the Royal Observatory of Uccle, Belgium. The advantages of this station are: its elevation of 11,700 ft. (3580 meters), the greatly reduced  $\text{H}_2\text{O}$  absorption, and the remoteness from large industries.

MIGEOTTE, M., AND NEVEN, L., "High-Dispersion Solar Spectrograms between 15  $\mu$  and 24  $\mu$ ," *Astrophys. J.* 115, 326 (1952).

The author's report in this brief note their observations of the solar spectrum between 15  $\mu$  and 24  $\mu$ .

The newly observed band,  $\nu_2$ , at 17  $\mu$  is attributed to nitrous oxide. The prism-grating spectrograph of the University of Liege was used in the observations. The spectrograph was equipped with an original echelette grating from the University of Michigan, having 1200 lines per inch. As receiver the authors used a Perkin-Elmer thermocouple which was connected to a Leeds and Northrup Speedomax Recorder through a 13-cycle Perkin-Elmer Electronic Amplifier.

MICOTTE, M., AND SEVEN, L., "Recent Progress in the Observation of the Solar Infrared Spectrum at Jungfraujoch (Switzerland)," *Mem. Soc. Roy. Sci., Liege*, 12, 165 (1952).

The identification of the following infrared absorption bands were identified on grating spectrograms.

CH <sub>4</sub>	3.3, 3.53, 3.9, 7.7 $\mu$ .
N <sub>2</sub> O	2.97, 2.97, 3.57, 3.9, 4.06, 4.5, 7.8, 8.6 $\mu$ .
CO <sub>2</sub>	4.3, 5.2, 6.3, 10.4, 13.9 $\mu$ .
CO	4.6 $\mu$ .
H <sub>2</sub> O	3.7 $\mu$ .
O <sub>3</sub>	9.5 $\mu$ .

SHAW, J. L., OXBORN, M. L., AND CLAASSEN, B. H., "The Solar Spectrum from 7  $\mu$  to 13  $\mu$ ," *Astrophys. J.* 116, 554 (1952).

In this paper the authors have reported their results upon reinvestigation of the infrared spectrum from 7 to 13  $\mu$  with a high-resolution grating spectrometer. Absorption bands of atmospheric H<sub>2</sub>O, CO<sub>2</sub>, O<sub>3</sub>, N<sub>2</sub>O and CH<sub>4</sub> are discussed individually. An extensive table of line frequencies and line identifications for this spectral interval in the solar spectrum is included. Also a map of the spectrum is shown.

Regarding the abundance of atmospheric N<sub>2</sub>O reference is made to the estimates reported by McMath and Goldberg (*Proc. Am. Phil. Soc.* 93, 362 (1949)) who give the value of about 0.4 atmo-cm. The authors state that this amount is sufficient for the fundamental at 7.8  $\mu$  to appear strongly in the solar spectrum and the overtone band 2  $\nu_2$  at 8.6  $\mu$  to be observed as a weak absorption. The  $\nu_1$  fundamental is the more intense band. However, it is obscured in the solar spectrum by overlapping bands of CH<sub>4</sub> and H<sub>2</sub>O. As a result only a few lines of N<sub>2</sub>O have been identified.

Many more lines of the much weaker 2  $\nu_2$  which lies in a comparatively transparent window have been observed. Many of the N<sub>2</sub>O lines in the 8.6  $\mu$  region are obscured by several intense H<sub>2</sub>O lines, especially during the summer months. Other polyatomic atmospheric constituents which included C<sub>2</sub>H<sub>4</sub> (11.9  $\mu$  band), C<sub>2</sub>H<sub>2</sub> (10.5  $\mu$ ), NH<sub>3</sub> (10.7  $\mu$ ), C<sub>2</sub>N<sub>2</sub> (4.6  $\mu$ ), SO<sub>2</sub> (8.6  $\mu$ ), NO (5.3  $\mu$ ), and NO<sub>2</sub> (3.4  $\mu$ ) were included in the studies. No indication of any absorption was found which was taken to mean that the abundance of these gases, if present in the atmosphere, must be considerably smaller than such minor constituents as CH<sub>4</sub> and N<sub>2</sub>O.

#### 1953

COOK, R., "The Vapor Pressure and Orthobaric Density of Nitrous Oxide," *Trans. Faraday Soc.* 49, 716 (1953).

The determination of the vapor pressure of nitrous oxide from 12°C to the critical point, and the orthobaric densities from 20°C to the critical point have been studied and reported in this paper. The experimental procedures including a description of the apparatus employed, the preparation of the gas, method of filling the pressure tube, and the results obtained are discussed in detail.

The vapor pressures were determined from the following relationship.

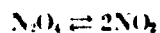
$$\log p(\text{atm}) = 4.6258 - (858.63/T).$$

Equations are also given for deriving the orthobaric densities. A graph of the orthobaric densities of N<sub>2</sub>O by various authors, the International Critical Tables, as well as the author's present measurements is included for comparison purposes. The present data are in good agreement with previous values.



FRIEDEL, R. A., SHARKEY, A. G., SHULTZ, J. L., AND HUMBERT, C. R., "Mass Spectrometric Analysis of Mixtures Containing Nitrogen Dioxide," *Anal. Chem.* 25, 1314 (1953).

This is an excellent paper by workers in the Synthetic Fuels Research Branch, Bureau of Mines, Bruce-  
ton, Pennsylvania. The erratic behavior of nitrogen dioxide in the mass spectrometer is due to chemical  
reactivity. The following equilibrium exists under normal temperature and pressure conditions.



In this study of the mass spectrum of  $\text{NO}_2$ , a Consolidated 21-103 Mass Spectrometer was used. The  
materials, apparatus, and method of procedure for analysis are fully described. Several curves of  $\text{NO}_2$   
mass spectral patterns at various pressures (microns), and  $\text{NO}_2$  mass spectral sensitivities at various pressures  
are included in the paper.

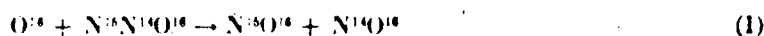
In the following table the mass spectra of nitric, nitrous oxide, and a comparison spectrum of nitrogen  
dioxide are shown:

Mass	NO	Patterns $\text{N}_2\text{O}$	$\text{NO}_2$
12	0.31	0.14	1.45
14	12.1	16.8	40.2
15	2.58	0.14	0.77
16	2.75	6.05	92.3
19.6	—	—	0.24 m
22	—	0 d	—
23	—	—	0.22 d
28	5.64	18.1	15.8
29	0.05	0.23	0.41
30	100	38.3	298
31	0.37	0.13	1.09
32	0.23	0.15	4.19
44	—	100	0.39
45	—	0.75	—
46	—	0.21	100
47	—	—	0.39
48	—	—	0.36
Sensitivity of parent mass, in divisions per micron (n-butane mass 58 sensitivity 7.73 divisions/micron).			
	44.6	33.0	9.10
m, metastable ion	d, doubly charged ion		

FRIEDMANN, LEWIS, AND BIGELEISEN, JACOB, "The Thermal Decomposition of Nitrous Oxide," *J. Am. Chem.  
Soc.* 75, 2215 (1953).

This is a study of the thermal decomposition of  $\text{N}_2\text{O}$  enriched with  $\text{N}^{15}\text{N}^{14}\text{O}$  and a subsequent search  
for possible equilibration of  $\text{N}^{14}$  and  $\text{N}^{15}$  in the nitrogen product. The decomposition reactions were per-  
formed in sealed cylindrical quartz vessels  $3 \times 10$  cm and a pressure of about 80 mm Hg at room temperature.  
The decomposition and exchange reaction temperatures were about 750°C. The samples and reaction  
products were analyzed with a mass spectrometer.

The decomposition of  $\text{N}_2\text{O}$  was complete in all cases. The results obtained showed that NO neither exchanges with  $\text{N}_2\text{O}$  nor catalyzes the equilibration of nitrogen during the decomposition of  $\text{N}_2\text{O}$ . The following reaction was considered to be the main source of NO.



Reference is made to the investigations of Noyes (1937) who suggested reaction (1) to account for the formation of NO in the photolysis of  $\text{N}_2\text{O}$ . The following unimolecular mechanism appeared to be consistent with the decomposition studies reported by the authors in the present paper.



GOLDBERG, LEO, AND MÜLLER, EDITH A., "The Vertical Distribution of Nitrous Oxide and Methane in the Earth's Atmosphere," *J. Opt. Soc. Am.* 43, 1033 (1953).

The authors state in the introduction that the vertical distribution of minor constituents of the earth's atmosphere has an important bearing on the question of their origin and photochemistry. The following methods for obtaining information on the vertical distribution are listed: (a) Direct sampling at various altitudes, (b) Results of chemical and spectroscopic analyses of the lower atmosphere compared with abundances derived for the whole atmosphere from studies of the solar spectrum, (c) Evidence on the vertical distribution may be inferred from spectroscopic abundances obtained from different sites and altitudes assuming that the geographical distribution is uniform, (d) The low-sun method which is based on the measurement of line intensities when the sun is close to the horizon.

The low-sun method is described in the present paper. The principle involved in this method is that in a curved atmosphere, the amount of absorbing gas traversed by a ray of sunlight from directions near the horizon depends upon the vertical distribution. The geometry of the curved atmosphere is described in detail.

The instrumentation employed was a high-dispersion spectrometer and Cashman PbS cell of the McMath-Hulbert Observatory attached to the Snow telescope at Mount Wilson. Four lines, P25, P26, P27, and P29 in the  $2.16\text{-}\mu$  band of  $\text{N}_2\text{O}$  were observed on 8-12 November and 28-29 November 1950. The total absorptions were measured with a planimeter.

The relative amounts of absorbing gas traversed by light rays coming from different zenith angles of the sun were calculated from the Link and Sekera tables (*Publ. Nat. Obs.* (Prague) 14 (1940)). The values in these tables are based on the observed density distribution in the atmosphere and take into account the refraction. Densities up to 20 km were taken from "Physics of the Air" by Humphreys, McGraw-Hill Book Company, Inc., New York (1940). Between 20 km and 45 km the densities were calculated from temperatures given by Ducert (*Erg. d. kosm. Physik* 1, 236 (1931)). For altitudes higher than 45 km the densities were obtained from the following references: Link (*J. des Observ.* 18, 161 (1934)) and Lindemann and Dobson (*Proc. Roy. Soc. (London)* A 102, 441 (1922)).

The quantity  $L_z/L_0$  was calculated, where  $L_z$  and  $L_0$  are the total amounts of absorbing gas in direction of the zenith angle,  $z$ , and through the zenith. The quantity  $L_z/L_0$  is the path length in air masses. It was assumed that the vertical distribution of nitrous oxide is concentrated in a layer of uniform density 5-km thick at altitudes 15, 25, and 50 km and that the  $N_2O$  on the above four assumptions as to vertical distribution are shown in Figure 4 in the paper.

The authors conclude that the line intensities for  $N_2O$  observed at low solar altitudes seem definitely to rule out the concentration of  $N_2O$  in layers at altitudes of 15 km or higher in the earth's atmosphere. The observations also show that  $N_2O$  is uniformly mixed with the major constituents and is concentrated in the lower levels of the atmosphere.

GOODY, R. M., AND WALSHAW, C. D., "The Origin of Atmospheric Nitrous Oxide," *Quart. J. Roy. Meteorol. Soc.*, 79, 496 (1953).

The authors discuss new observational data which indicate that:

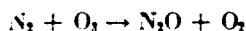
- (a) Nitrous oxide is uniformly mixed with the atmosphere up to 10 km and probably to 40 km. The volume mixing ratio is  $3.5 \times 10^{-7}$ .
- (b) Bacterial reactions in the soil can supply nitrous oxide to the atmosphere at a rate sufficient to compensate photo-chemical decomposition.
- (c) The formation of nitrous oxide by homogeneous chemical reactions is probably of less importance.
- (d) The average magnitude of the nitrogen cycle between earth and atmosphere is probably not less than  $10^{11}$  molecules  $cm^{-2} sec^{-1}$ .

It is stated that nitrous oxide is the only oxide of nitrogen whose presence in the atmosphere has been established by direct observational evidence. Reference is made to the six records of the  $7.8 \mu$  bands of  $N_2O$  in the solar spectrum obtained on aircraft flights over Southern England by Yarnell and Goody (*J. Sci. Instr.*, 29, 352 (1952)). The altitudes were between 3 km and 8 km. Aircraft results were consistent with a constant mixing ratio of  $2.7 \pm 0.8 \times 10^{-7}$  by volume between 3 km and 10 km. The spectra from Arizona were consistent with a volume mixing ratio of  $4.0 \pm 0.5 \times 10^{-7}$ . The results from Arizona were obtained at an altitude of 2.21 km. The results of Slobob and Krogh (1950) at ground level in Texas from mass spectroscopic measurements gave values from  $2.5$  to  $6.5 \times 10^{-7}$ .

The natural lifetime of a molecule of nitrous oxide to photodissociation according to Bates and Witherspoon is shown in the following table.

Altitude Km	10	20	30	40	60
Lifetime (days)	4000	800	50	20	10

With reference to bacterial reactions in the soil the authors state that by using the best available data, a time constant of 200 days is required to supply an average over the whole globe of  $8 \times 10^{10}$  nitrous oxide molecules  $cm^{-2} sec^{-1}$ . This demonstrates that bacterial reactions could supply the nitrous oxide in the atmosphere. Reference is made to Bates and Witherspoon (1952) who examined possible mechanisms by which nitrous oxide could be produced by homogeneous chemical reactions. The following was considered most promising.



A rate coefficient of  $5 \times 10^{-17} \text{ cm}^3 \text{ sec}^{-1}$  was considered to be adequate to account for the nitrous oxide in the atmosphere.

Goody and Walshaw state that they were able to make an estimate of the rate of the above reaction by mixing nitrogen and ozone in an absorption tube, measuring the ozone decay from the absorption in the Chappuis band and the nitrous oxide formed from the intensity in the  $7.8 \mu$  band. In three experiments which were performed, one showed a weak doublet of the right shape at  $7.8 \mu$  from which the nitrous oxide density could be estimated to be  $1.5 \times 10^{13} \text{ molecules cm}^{-3}$ . The rate coefficient was deduced to be less than or equal to  $5 \times 10^{-18} \text{ cm}^3 \text{ sec}^{-1}$  at  $19^\circ\text{C}$ . The analysis of the interpretation, wall reaction effect, and similar topics are discussed.

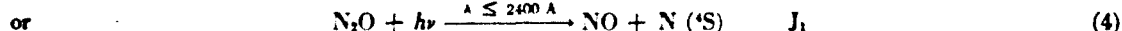
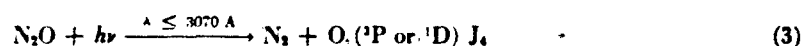
The conclusion of Goody and Walshaw although not greatly different from that of Bates and Witherspoon reverse the emphasis and consider bacterial reactions in the soil to be a possible source of atmospheric nitrous oxide while the homogeneous gas reaction is probably of secondary importance. The evidence obtained by Goody and Walshaw indicates that the homogeneous gas reaction mechanism proposed by Bates and Witherspoon is too slow by a factor of 40 to account for the observed concentration of nitrous oxide in the atmosphere.

MITRA, A. P., "A Tentative Model of the Equilibrium Height Distribution of Nitric Oxide in the High Atmosphere and the Resulting D-Layer." Ionospheric Research. Scientific Report No. 46. The Pennsylvania State College, 15 May 1953. AMC Contract No. AF19(122)-44.

With reference to the mechanism of production of  $\text{N}_2\text{O}$ , the author reviews the discovery by Slobod and Krogh who originated the suggestion that atmospheric  $\text{N}_2\text{O}$  is produced in the soil by some micro-organisms. Reference is also made to Bates and Witherspoon who considered that the atmospheric  $\text{N}_2\text{O}$  might result from homogeneous gas reactions at low atmospheric levels. The following reactions were considered favorable by Bates and Witherspoon.



The parent particles O and  $\text{O}_3$  might be produced with sufficient rapidity to compensate for the rapid destruction rate of  $\text{N}_2\text{O}$  by the following photochemical reactions.



The values of  $J_1$  and  $J_4$ , the photodissociation coefficients were calculated by Bates and Witherspoon for a number of heights.

Mitra in the present report considers both reactions (1) and (2) giving the following rate equations.

$$\frac{dn_1(\text{N}_2\text{O})}{dt} = k_4 n(\text{N}_2) n(\text{O}) n(\text{M}) - (J_1 + J_4) n(\text{N}_2\text{O}) \quad (5)$$

$$\frac{dn_2(\text{N}_2\text{O})}{dt} = k_5 n(\text{O}_3) n(\text{N}_2) - (J_1 + J_4) n(\text{N}_2\text{O}) \quad (6)$$

Under equilibrium conditions, the corresponding concentrations of  $N_2O$  would be

$$n_1(N_2O) = \frac{k_4 n(N_2) n(O) n(M)}{J_1 + J_4} \quad (7)$$

and

$$n_2(N_2O) = \frac{k_5 n(O_2) n(N_2)}{J_1 + J_4} \quad (8)$$

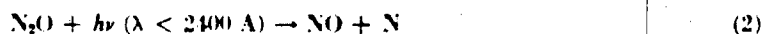
In Table III (A), (B) and (C) in the report the values of the various parameters used are given for heights from 50 km to 100 km. From these values the height distribution of  $N_2O$  was calculated for the region 50–100 km. From the distributions of  $N_2O$  and  $N$ , Mitra uses these values to calculate the height distribution of nitric oxide (NO).

$$n(NO) = \frac{k_1 n(N) n(O) n(M) + J_1 n(N_2O)}{k_2(T) n(N) + J_1} \quad (9)$$

NICOLET, MARCEL, "Aeronomical Problem of Nitrogen Oxides," Ionosphere Research. Scientific Report No. 52, The Pennsylvania State College, 25 October 1953, AMC Contract No. AF19(122)-44.

With reference to nitrous oxide its observation and discovery from infrared studies by Adel (1939), Migeotte (1948), Shaw, Sutherland, and Wormell (1948) are mentioned. Also reference is made to the abundance of the order of  $10^{11}$  molecules  $cm^{-2}$  found by McMath and Goldberg (1949), and Migeotte, Benesch and Neven (1953); and the vertical distribution by Goldberg and Muller (1953).

Reference is made to the study of the photochemistry of tropospheric nitrous oxide by Bates and Witherspoon (1952) who found that the  $N_2O$  molecule is not a member of the main photochemical series of nitrogen oxides. Mitra (Scientific Report No. 46, Pennsylvania State College (1953)) has proposed the following mechanisms for the formation and photodissociation of  $N_2O$ .



Mitra (1953) considered reaction (1) as the source of nitrous oxide at mesopause levels, and also gives the following reaction:



as another possibility for its production. The latter process had been suggested by Bates and Witherspoon (1952).

Nicolet in the present report considers the source of  $N_2O$  at mesopause levels to be process (1) rather than process (3) because of the high activation energy in the latter mechanism. The author gives a quantitative discussion of nitrous oxide and atmospheric oxygen system in which the following equation of the rate formation is given.

$$\frac{\delta n(N_2O)}{\delta t} = k_4 n(N_2) n(O) n(M) \quad (4)$$

(The above equation is obtained from (1). The following process is also considered.



It is stated that process (5) would be associated with the altitudes near the mesopause. Assuming a value of  $10^6 \text{ cm}^{-2}$  for the product of  $n(N_2) n(O) n(O_2)$ , a yield of 50 photons  $cm^{-2} \text{ sec}^{-1}$  would correspond to

a rate coefficient of  $5 \times 10^{-33} \text{ cm}^3 \text{ sec}^{-1}$  for the excitation process of the atmospheric bands of  $\text{O}_2$ . Bates and Witherspoon (1952) and Bates (1952) who discussed process (5) concluded that the rate coefficient for the reaction would not be expected to have a value greater than  $1 \times 10^{-33} \text{ cm}^3 \text{ sec}^{-1}$ . Nicolet concludes that both theoretical and experimental investigations have not as yet yielded reliable data to calculate the rate coefficient.

THOMPSON, H. W., AND WILLIAMS, R. L., "Vibration Bands and Molecular Rotational Constants of Nitrous Oxide," *Proc. Roy. Soc. (London)* A 220, 435 (1953).

The authors have reported the measurement of seven vibration-rotation bands of nitrous oxide. The rotational line structure of each band was analyzed. The three fundamental vibration frequencies,  $\nu_1$ ,  $\nu_2$ , and  $\nu_3$ , were found to be approximately 1285, 589, and  $2223.5 \text{ cm}^{-1}$ . The values for rotational constants were derived. The value for  $B_{v=0}$  was found to be  $0.4190 \text{ cm}^{-1}$  from four bands as compared to  $0.4191$  found by Herzberg and Herzberg. The values for the coefficient  $\alpha_1$  for the different vibrational levels are also reported.

ZELIKOFF, MURRAY, WATANABE, K., AND INN, EDWARD C. Y., "Absorption Coefficients of Gases in the Vacuum Ultraviolet, Part II, Nitrous Oxide," *J. Chem. Phys.* 21, 1643-1647 (1953).

In this paper the authors report their measurements of the absorption coefficients of  $\text{N}_2\text{O}$  in the region  $\lambda$  1080-2100 Å.

Four continua were observed at 1820 Å, 1450 Å, 1285 Å, and 1080 Å. The  $f$  values were 0.0015, 0.0211, 0.367, and 0.1 respectively.

The strongest band areas found for absorption were observed to lie at 1178 Å with an absorption coefficient of  $3010 \text{ cm}^{-1}$  at its maximum.

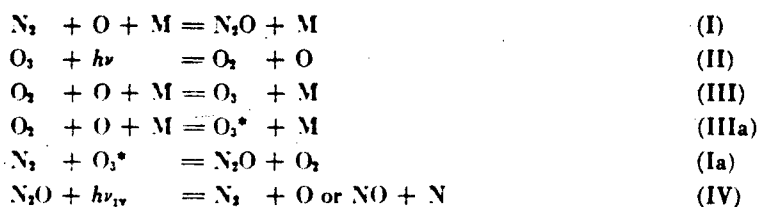
#### 1954

DOUGLAS, A. E., AND MÖLLER, C. K., "The Near-Infrared Spectrum and the Internuclear Distance of Nitrous Oxide," *J. Chem. Phys.* 22, 275 (1954).

The authors have reported the results of their study of the spectra of the isotopic mixture of nitrous oxide,  $\text{N}_2^{14}\text{O}^{16}$  and  $\text{N}_2^{14}\text{N}^{14}\text{O}^{16}$ . From the  $B_v$  values the equilibrium internuclear distances were found. The internuclear distance,  $\text{N} - \text{N}$  is given as 1.126 Å, and the  $\text{N} - \text{O}$  distance 1.186 Å.

HARTECK, P., AND DONDES, S., "Origin of Nitrous Oxide in the Atmosphere," *Phys. Rev.* 95, 320 (1954).

The authors suggest that the presence of nitrous oxide in the atmosphere is due to photochemical equilibrium between nitrous oxide formation and nitrous oxide decomposition through the following mechanism:

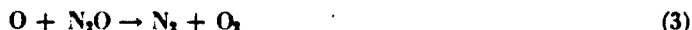


Reaction (1) above was accomplished by the authors and reported (*J. Chem. Phys.* 22, 758 (1954)) to have a heat of activation of only about 12 kcal. Assuming the sum of the light quanta absorbed by ozone as,  $h\nu_{\text{O}_3} = 5 \times 10^{15} \text{ cm}^2 \text{ sec}$  the nitrous oxide production was calculated, and, in turn, was found to be equivalent to the photochemical decomposition in the stationary state. Another possible reaction of nitrous oxide in the atmosphere being investigated by the authors (*J. Chem. Phys.* 22, 953 (1954)) is its formation from nitrogen dioxide.



ZELIKOFF, MURRAY, AND ASCHENBRAND, LEONARD M., "Vacuum Ultraviolet Photochemistry. I. Nitrous Oxide at 1470 Å," *J. Chem. Phys.* 22, 1680 (1954).

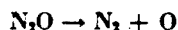
The authors report their study of the photolysis of nitrous oxide ( $\text{N}_2\text{O}$ ) at a wavelength of 1470 Å. The light source employed was the radiation from a xenon resonance lamp. The authors suggest that from their study of absorption by  $\text{N}_2\text{O}$  at  $\lambda$  1470 Å and in the spectral region 1950 Å to 1850 Å, nitrous oxide dissociates into molecular nitrogen and atomic oxygen. The following mechanism is considered most favorable for this dissociation.



The quantum yields were determined to be,  $\text{N}_2\text{O} = 1.7$ ,  $\text{O}_2 = 0.5$ , and  $\text{N}_2 = 1.4$ . The quantum yield for NO was found to be pressure-dependent.

ZELIKOFF, MURRAY, AND ASCHENBRAND, LEONARD M., "Vacuum Ultraviolet Photochemistry. II. Nitrous Oxide at 1849 Å," *J. Chem. Phys.* 22, 1685 (1954).

In this second paper Zelikoff and Aschenbrand in the study of the photochemistry of nitrous oxide in the vacuum ultraviolet employed a low-pressure Hg arc as a source of radiation. The quantum yield ratios reported are,  $\text{N}_2\text{O} : \text{N}_2 = 1.24$ ;  $\text{N}_2\text{O} : \text{O}_2 = 3.47$ ; and  $\text{N}_2\text{O} : \text{NO}$  was found to be pressure dependent. The evidence obtained from the spectroscopic data appears to support the assumption that initially the process of photodissociation of  $\text{N}_2\text{O}$  leads to the formation of nitrogen molecules and atomic oxygen,



and that nitric oxide (NO) is produced by the reaction,



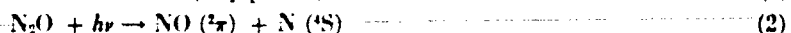
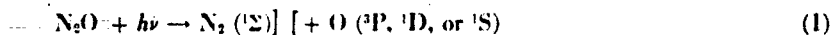
#### 1955

AMAT, G., BARCHEWITZ, P., AND GRENIER-BESSON, M.-L., "A Preliminary Study of the Spectra of  $\text{N}_2\text{O}$  under Great Thickness between 1.5 and 2.5  $\mu$ ," *J. phys. radium* 16, 16 (1955).

The authors report a preliminary study of the vibration-rotation spectra of nitrous oxide ( $\text{N}_2\text{O}$ ) between 1.5 and 2.5  $\mu$ . A brief description of the instrumentation is given. A certain number of new bands of weak intensity were observed. The determination of suitable frequencies of corresponding vibrations permitted the calculation of vibrational constants of this molecule.

CVEFANOVIC, R. J., "Mercury Photosensitized Decomposition of Nitrous Oxide," *J. Chem. Phys.* 23, 1203 (1955).

The decomposition of nitrous oxide induced by direct photochemical decomposition in the far ultraviolet is briefly reviewed. The investigations of Macdonald (1928), Noyes (1937) and Henriques and others (1938) are cited. According to Zelikoff, Watanabe, and Inn (1953) the accessible electronic levels of nitrous oxide are repulsive and the following are possible primary processes.



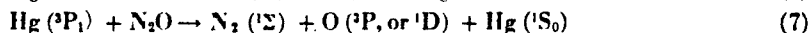
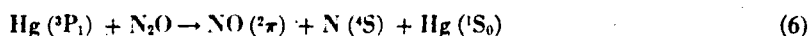
Noyes (1937) considered the large amounts of nitric oxide produced to be the result of the reaction



and concluded that the primary process (1) was accompanied by (2) and followed by the reactions



The experimental instrumentation and procedure of the author's method are described in detail. The reaction was studied by analyzing the products and by following the change in the amount of transmitted light during the process. Nitrogen and oxygen very close to the stoichiometric ratio of 2 : 1 were the major and almost exclusive products of the reaction. The following two primary processes were considered possible.



It was concluded that reaction (7) was by far the predominant and possibly the exclusive step. The author states that the results of his present experiments support the view expressed previously by Noyes (1937). There was indication of recombination of oxygen atoms. The latter reaction was catalyzed by the small amounts of higher nitrogen oxides formed as secondary reaction products.

KAUFMAN, FREDERICK, AND KELSO, JOHN R. "Reaction between Nitric and Nitrous Oxide," *J. Chem. Phys.* 23, 602 (1955).

Reference is made to Muirgrave and Hinshelwood (*Proc. Roy. Soc. (London)* A 135, 23 (1932)) who first studied the catalytic effect of nitric oxide in the decomposition of nitrous oxide. The temperature range of the present investigation was 924 to 1028°K. The reaction was found to be accurately first order in both NO and N<sub>2</sub>O. The following table is included.

Determination of Order in N <sub>2</sub> O				
T = 924°K		p <sub>NO</sub> = 100 mm Hg p <sub>O<sub>2</sub></sub> mm Hg		t = 30 sec
p <sub>N<sub>2</sub>O</sub> mm Hg	Total	N <sub>2</sub> O blank	Δ	$\frac{\Delta p_{\text{O}_2}}{p_{\text{N}_2\text{O}}} \times 10^3$
25	0.491	0.059	0.432	1.728
50	1.024	0.164	0.860	1.720
100	2.224	0.460	1.764	1.764
200	4.70	1.29	3.51	1.755

The order in NO was obtained by plotting  $1/t \times \log \{[\text{N}_2\text{O}]_0/[\text{N}_2\text{O}]_t\}$  vs p<sub>NO</sub> at constant p<sub>N<sub>2</sub>O</sub>. The



authors conclude that the importance of the NO catalyzed decomposition of  $N_2O$  decreases with increasing temperature, the activation energy of the uncatalyzed reaction being greater than 50 kcal.

WALKER, W. C., AND G. L. WEISSLER, "Photoionization Efficiency and Cross Sections in  $N_2O$  and NO," *J. Chem. Phys.* 23, 1962 (1955).

The authors have reported in the present paper preliminary measurements of total absorption cross sections, photoionization efficiencies, and ionization cross sections of  $N_2O$  and NO in the region between the ionization onset and 687 Å. It is stated that absorption spectra for  $N_2O$  have been obtained to 850 Å by Duncan (*J. Chem. Phys.* 4, 638 (1936)) and that absorption coefficients have been measured to 100 Å by Zelikoff, Watanabe and Inn (*J. Chem. Phys.* 21, 1643 (1954)). No absolute measurements have been published for the region of the ionization continuum of  $N_2O$ . Watanabe (*J. Chem. Phys.* 22, 1564 (1954)) has reported absolute absorption and ionization measurements of NO in the region from the ionization onset to 1080 Å.

The authors in the present letter to the editor have shown the photoionization efficiencies of  $N_2O$ . An ionization onset was obtained at  $965 \pm 5$  Å ( $12.83 \pm 0.07$  eV). The absorption and ionization cross sections for  $N_2O$  were observed to be independent of pressure except for four lines at 770, 707, 833 and 843 Å where the cross sections increased with decreasing pressure.

The ionization onset of NO was found at  $1347 \pm 5$  Å ( $9.20 \pm 0.03$  eV) in agreement with  $9.25 \pm 0.02$  eV reported by Watanabe. Fluctuations in the cross sections with wavelength were interpreted to indicate the presence of diffuse bands in the region below 1000 Å in agreement with absorption spectra obtained by Tanaka (*J. Sci. Research Inst. (Tokyo)* 43, 16 (1949)).

## 2.2 NITRIC OXIDE NO

1926

LEIFSON, SIGMUND W., "Absorption Spectra of Some Gases and Vapors in the Schumann Region," *Astrophys. J.* 63, 73 (1926).

In this study the author has reported his results of absorption spectra of gases in the Schumann region. In regard to NO absorption measurements were made at pressures of 0.01, 0.1 and 1.0 atmosphere. A large number of narrow absorption bands was observed and photographed. The spectrograms for NO are shown in Plate IV in the paper. The bands and band groups are listed in Tables V and VI.

The instrumentation consisted of a vacuum spectrograph with an absorption cell with fluorite windows built into the discharge tube. The fluorite window transmitted the hydrogen line  $\lambda$  1215.67 (Lyman alpha) which was apparently a new ultraviolet limit for the transparency of fluorite. The author acknowledges his indebtedness to Dr. J. J. Hopfield and to Professor R. T. Birge. A list of sixteen references to previous investigations of the gases studied are included.

1927

BARTON, HENRY A., JENKINS, FRANCIS A., AND MULLIKEN, ROBERT S., "The Beta Bands of Nitric Oxide. II. Intensity Relations and their Interpretation," *Phys. Rev.* 30, 175 (1927).

In this paper the authors report their results in testing the equations of Hönl and London (*Z. Physik* 33, 803 (1925)) predicting the relative intensities of band spectrum lines with the beta bands of NO ( $^2P \rightarrow ^2P$  transition), a system emitted by an odd molecule. Both comparison of line intensities and intensity between bands are considered.

JENKINS, FRANCIS A., BARTON, HENRY A., AND MULLINEN, ROBERT S., "The Beta Bands of Nitric Oxide. I. Measurements and Quantum Analysis," *Phys. Rev.* 30, 150 (1927).

This is an extensive and useful paper upon the band structure and wave-number data of the  $\beta$ -bands of NO. The spectral region  $\lambda\lambda$  2300 Å to 5300 Å was photographed in the second order of a 21-foot Rowland concave grating.

Various constants of the nitric oxide molecule, such as moment of inertia, internuclear distance, are included. The experimental procedure is described in detail. The analysis of the band structure and the description of the bands receive extensive discussion.

#### 1930

LAMBREY, MAURICE, "Spectroscopic Investigations of Nitric Oxide and Nitrogen Dioxide," *Ann. Phys.* 14, (Ser. 10), 95-184 (1930).

This is an extensive study of the absorption spectra of nitric oxide and nitrogen dioxide. The absorption spectrum was photographed using a small quartz spectrograph. Hydrogen was used as a continuous light source. The spectra of NO was found to have two systems of doublets. The most intense was the  $\gamma$ -system extending from 2368.6 Å to 1871 Å, while the  $\beta$ -system extended from 2210.5 Å to 1908 Å. The coefficient of absorption of NO was determined between  $\lambda\lambda$  2400-2100 Å. It was found that the introduction of a foreign gas caused an increase in the absorption coefficient.

The absorption spectra of nitrogen dioxide (NO<sub>2</sub>) was also studied in the ultraviolet. The spectra was found to consist of two wide bands due to nitrogen tetroxide (N<sub>2</sub>O<sub>4</sub>). Other bands were of a complex structure and were attributed to NO<sub>2</sub>.

#### 1931

KAPLAN, JOSEPH, "Repulsive Energy Levels in Band Spectra," *Phys. Rev.* 37, 1406 (1931).

In this paper the author gives an explanation for many cases of anomalous intensity distribution in the band spectra of diatomic molecules. Some of the examples discussed are: NO, N<sub>2</sub> and CO.

The following values are given for the heats of dissociation of N<sub>2</sub>, O<sub>2</sub> and NO: N<sub>2</sub> = 9.1 volts, O<sub>2</sub> = 5.06 volts, and NO = 6.15 volts.

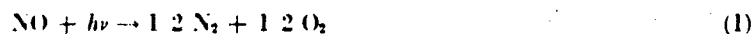
In regard to nitric oxide it is stated that the beta bands of nitric oxide possess a very exceptional intensity distribution. To explain these anomalies the author postulates an interaction between the excited states of NO on which the beta bands arise and the Heitler and London level corresponding to the coming together of normal atoms of nitrogen and oxygen. The failure of the beta bands to obey the Franck-Condon rule for band intensities is given as evidence that the postulate is correct.

#### 1935

FLORY, PAUL J., AND JOHNSTON, HERRICK L., "The Photochemical Decomposition of Nitric Oxide," *J. Am. Chem. Soc.* 57, 2641 (1935).

The photochemical decomposition of nitric oxide by radiation from the mercury arc and with sparks between various metal electrodes, and over a pressure range from 0.02 to 7 mm was investigated. The metal electrodes employed were: aluminum, zinc, cadmium, nickel, copper and tin.

The authors conclude that the final decomposition products are nitrogen and oxygen. The latter substance is removed by reaction which takes place during compression of the gas in the McLeod gage. The successive stoichiometric reactions for the decomposition mechanism are given as follows:

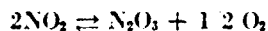


No radiation below  $\lambda 1750 \text{ \AA}$  was considered to enter into the photochemical reaction cell. The use of filters containing solutions of ammonium chloride and ammonium hydroxide places the effective radiation from the mercury arc below  $\lambda 1900 \text{ \AA}$ . The use of a water filter gave indication that the effective spectral region is in the neighborhood of  $\lambda 1830 \text{ \AA}$ . The strong resonance line at  $\lambda 1849 \text{ \AA}$  was ruled out. It was concluded that absorption in the  $\delta(1, 0)$  band of nitric oxide together with some absorption in the bands of the  $\beta$ -system was responsible for the dissociation process. Since the active radiation is in a banded spectral region of nitric oxide the dissociation process was thought to be one of predissociation. This interpretation is supported by the investigations of Kaplan (*Phys. Rev.* 37, 1406 (1931)) since it agrees with the evidence for predissociation provided by the emission spectrum of nitric oxide. Several stoichiometrically possible secondary processes are also considered all of which were ruled out from experimental and theoretical considerations.

MELVIN, EUGENE H., AND WULF, OLIVER R., "Ultraviolet Absorption of Mixtures of NO, NO<sub>2</sub> and H<sub>2</sub>O," *J. Chem. Phys.* 3, 755 (1935).

Included in this paper are three spectrograms showing absorption bands of mixtures of NO, NO<sub>2</sub> and H<sub>2</sub>O together with effects produced upon the appearance of the absorption bands by (a) increasing the amount of nitrogen dioxide, (b) the effect of nitric oxide, (c) the effect of increasing water, and (d) the effect of increasing temperature. The conditions for obtaining these pictures are fully described.

The authors raise a pertinent question as to the N<sub>2</sub>O<sub>3</sub> content of "pure NO<sub>2</sub>." In a mixture of pure 2NO<sub>2</sub>  $\rightleftharpoons$  N<sub>2</sub>O<sub>4</sub> as one can prepare there exists the following equilibrium:



1938

KAPLAN, JOSEPH, "The Preparation and Properties of Auroral Afterglows," *Phys. Rev.* 54, 176 (1938).

The preparation of auroral afterglows showing the various stages is described. The discharge tube consisted of a central pyrex or quartz bulb (100 ml to 5 liters) with pyrex side tubes which contained aluminum electrodes.

Five distinct stages may usually be observed in the preparation of the glow tube when carbon and oxygen are present as impurities. These are called (1) the ozone stage, (2) nitric oxide stage, (3) cyanogen stage, (4) Lewis-Rayleigh afterglow, and (5) the auroral stage.

The afterglow of nitric oxide (NO) stage is blue in color and its spectrum is characterized by the presence of the  $\beta$ -bands of NO in the visible and ultraviolet and the  $\gamma$ -bands in the ultraviolet. Photographs are shown of the afterglows, one of which includes the nitric oxide stage.

1939

CHAPMAN, SYDNEY. "Spectroscopic and Other Evidence as to Chemical Composition and Dissociation. The Upper Atmosphere." *Quart. J. Roy. Meteorol. Soc.* 65, 310 (1939).

In this paper read at the Joint Meeting of the Chemical Society, the Physics Society, and the Royal Meteorological Society on 4 May 1939 at the Royal Institution London, Chapman discussed the problem of the composition of the atmosphere above 100 or 150 km altitude.

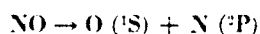
Evidence from the spectrum of the auroral light, which is emitted to strong excitation of the air particles by fast moving corpuscles coming from the sun, seems to indicate that everywhere up to 600 km the atmosphere is a nitrogen-oxygen atmosphere. Both the auroral and night sky emission spectra show bands due to molecular nitrogen, both neutral and ionized. The author states that lines due to atomic oxygen are prominent in both the night sky and auroral spectra, but bands due to molecular oxygen are missing in both spectra.

KAPLAN, JOSEPH. "Nitric Oxide in the Earth's Upper Atmosphere," *Nature* 144, 152 (1939).

In this letter to *Nature* the author states that one of the most conspicuous characteristics of nitrogen afterglow spectra is the intense excitation of the  $\beta$ - and  $\gamma$ -systems of NO in active nitrogen even in the presence of only a trace of oxygen. The  $\beta$ -bands are more intense. The strongest members of this series lie on the long wavelength side of the great Hartley absorption band of ozone, while the  $\gamma$ -bands lie on the short wavelength side.

A spectrum of an afterglow produced by passing an extremely weak discharge through nitrogen at a pressure of 10 mm is shown in the paper. The nitrogen contained a trace of oxygen. The strong auroral afterglow appeared by applying a strong discharge. The spectra of the strong and weak afterglows were as different as those of the aurora and the light of the night sky. The Vegard-Kaplan bands  $\lambda$  3467 and the green auroral line are strong in the weak glow but almost absent from the strong afterglow. The latter consists of bands typical of auroral spectra.

The NO bands were entirely absent from the strong afterglow but appeared very strongly in the weak afterglow. From these laboratory experiments the author concluded that nitric oxide bands are present in the light of the night sky but are not observable due to ozone absorption. It is also pointed out that nitric oxide must play an important part in excitation processes in upper atmospheric spectra. The following process is postulated:



The altitude of 25 km, the height of maximum ozone concentration, is suggested for the height of this reaction.

1941

ELVEY, C. T., SWINGS, P., AND LINKE, WALTER. "The Spectrum of the Night Sky," *Astrophys. J.* 93, 337 (1941).

In regard to the NO molecule the authors state that the spectrum of the NO molecules has usually been considered to be missing from the night sky. In the following table the authors give coincidences of night sky lines with  $\gamma$ -bands of NO:

$\lambda$ Laboratory	$\lambda$ Night Sky
(1-8), 3112	(3110)
(3-12), 3303	3298 3 (3) wide diffuse
(0-8), 3375	3378 2 (5) wide violet edge sharp
(1-10), 3458	3460 1 (2) narrow

It is stated that the presence of the  $\beta$ -bands of NO in the night sky is not ascertained, nor has it been excluded. The excitation potential is 5.6 volts. The  $\gamma$ -bands give coincidences as listed in the above table. However not too much weight should be given to these coincidences. The excitation potential required is 5.5 volts.

## 1942

ELVEY, C. T., "The Light of the Night Sky," *Rev. Mod. Phys.* 14, 140 (1942).

This is a paper presented at the Conference on Spectroscopy held at the University of Chicago 22-25 June 1942. The author states that in the short wavelength region in the spectrum of the night sky most of the radiations have been accounted for except for the strongest band in the ultraviolet region which is still somewhat uncertain. These radiations are all associated with molecules and none with atoms. The nitrogen molecule is the principal contributor.

In regard to the oxides of nitrogen Elvey states that only one, NO, seems to have any probability of being represented in the spectrum of the non-polar aurora. Both the  $\beta$ -bands and the  $\gamma$ -bands of NO may be present. The excitation potentials for these are 5.6 and 5.5 volts, respectively.

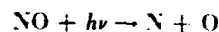
In summarizing the paper the spectrum of the non-polar aurora indicates that the following excited atoms and molecules are present in the upper atmosphere:

- (1)  $^1S$  and  $^1D_2$  states of oxygen.
- (2)  $^2P$  state of sodium.
- (3) The  $A\ ^2\Sigma$ ,  $B\ ^3\Pi$ ,  $A\ ^1\Pi$  states of the nitrogen molecule.
- (4) Probably the  $A\ ^2\Sigma$  and the  $B\ ^3\Pi$  states of the NO molecule.
- (5)  $B\ ^3\Sigma$  state of the oxygen molecule.
- (6) Certain excited states of the water molecule.

BAMFORD, C. H., "Photochemical Processes in an Oxygen-Nitrogen Atmosphere. IV. Nitric Oxide," *Reports Prog. Phys.* 9, 80 (1942-43).

The absorption spectrum of NO consists of a number of band systems from  $\lambda$  2250 Å to shorter wavelengths. There is no evidence of a continuum down to about  $\lambda$  1300 Å.

Reference is made to photolysis studies of nitric oxide by Macdonald (1928), and Flory and Johnston (1935). It was shown by Flory and Johnston that the rate of decomposition was independent of the pressure of NO, or added inert gas ( $N_2$ ). The effective wavelength is 1832 Å at low pressures ( $\delta$ -band), while above 33 mm Hg the wavelength 1849 Å ( $\beta$ -band) becomes important. At low pressures the following process occurs:



This reaction requires about 122 kcal, corresponding to a wavelength of about 2320 Å.

PEARSE, R. W. B., "The Spectrum of the Night Sky," *Reports Prog. Phys.* (London) 9, 42 (1942-43)

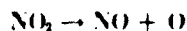
Apart from the atomic lines in the spectrum of the night sky, probably most of the remaining radiations are due to molecules. In regard to the presence of nitric oxide in the spectrum of the night sky the author states that the bands of the  $\gamma$  system,  $A\ ^2\Sigma \rightarrow X\ ^3\Pi$ , of NO are degraded to the violet. The system is readily obtained in the laboratory in a discharge tube; however, all the strongest bands are too far to the ultraviolet to provide a sensitive test for NO in the night sky. The degree to which night sky bands of approximate to

observed bands in the two systems of NO are given in Table I in the paper together with other molecular constituents.

PRICE, W. C., "Absorption Spectra and Absorption Coefficients of Atmospheric Gases," *Reports Prog. Phys.* (London) 9, 10 (1942-43).

The object of the present paper is to review the work on the electronic spectra and absorption coefficients of the atmospheric gases. The following oxides of nitrogen are considered:  $N_2O$ , NO,  $NO_2$ ,  $N_2O_3$ ,  $N_2O_4$ , and  $NO_3$ .

Nitric oxide may be quite an important atmospheric constituent, since it is formed from the photodissociation of nitrous oxide, and by the reaction of nitrous oxide molecules with oxygen in the presence of a third body. Also any nitrogen dioxide ( $NO_2$ ) present in the atmosphere is likely to be converted to nitric oxide, especially during daytime. The following reaction is probable with high light intensities and low pressures.



According to Leifson (*Astrophys. J.* 73 (1926)) the absorption spectrum of nitric oxide begins at 2270 Å. In the neighborhood of 1400 Å which corresponds to the first ionization potential for NO, 9.1 ev the bands are weaker and crowded together.

The author states that there is no phot ionization continuum here and little absorption to shorter wavelengths. A mechanism is suggested in which nitrogen molecules combine with oxygen atoms to yield nitrous oxide. The latter gives nitric oxide either by photochemical decomposition or by collision with an oxygen atom in the presence of a third body. The nitric oxide thus formed decomposes photochemically to give molecular nitrogen and oxygen.

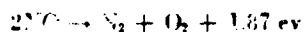
#### 1944

GAYDON, A. G., AND PENNY, W. G., "The Dissociation Energies of CO,  $N_2$ , NO, and CN," *Proc. Roy. Soc.* (London) A 183, 374 (1944).

In this communication the authors state that no previous set of values of the dissociation energies of CO,  $N_2$ , NO and CN can be regarded as satisfactory unless violations of the non-crossing rule are postulated as possible.

The Birge-Sponer extrapolation is discussed. By this method when a number of vibrational energy levels of a molecular state are known, extrapolation of these levels to the convergence limit correlated with the energy of dissociation of that particular state is possible. The authors conclude that there is little evidence that this method, when made with reasonable care, would be seriously in error for ground electronic states.

The non-crossing rule of Hund, and Newmann and Wigner (*Phys. Z.* 30, 467 (1929)) is discussed and illustrated. In regard to the dissociation of nitric oxide it is linked with that for nitrogen and oxygen by thermochemical data according to Bichowsky and Rossini ("The Thermo-chemistry of the Chemical Substances," New York, Reinhold (1936)).



Taking  $D(O_2) = 5.082$ , and  $D(N_2) = 9.56$ , the value of  $D(NO) = 6.49$  is obtained as compared to the lower value of 5.29 given by Herzberg (1939).

Gaydon (*Proc. Phys. Soc. (London)* 56, 160 (1944)) has studied the several band systems emitted by NO and drew up potential energy curves for all the known electronic states. The new value  $D(\text{NO})$  in the present paper lies just above all the known energy levels for the  $\beta$ ,  $\gamma$  and  $\delta$  systems. The non-crossing rule is, accordingly, not actually violated which would be difficult to reconcile for the low value 5.29 of Herzberg for  $D(\text{NO})$ .

KIESSELBACH, RICHARD, "Microdetermination of Nitric Oxide in Gases," *Anal. Chem.* 16, 766 (1944).

Since nitric oxide is insoluble and generally inert in character the method of determination involves a preliminary oxidation to the more soluble nitrogen dioxide. The method described in this paper consisted in passing the gas through an alkaline permanganate solution in a specially designed scrubber. The nitrogen dioxide obtained from the oxidation was analyzed by the micro Devarda method which is described by Kieselbach in the paper immediately preceding (*Anal. Chem.* 16, 764 (1944)).

Devarda's alloy reduces the nitrogen dioxide to ammonia which is absorbed in boric acid and titrated with 0.01 N HCl to bromocresol green-methyl red end-point. Descriptions of the experimental apparatus, procedure, precision and accuracy, interfering substances, and calculations are given in detail. For the highest precision and accuracy the sample should be large enough to contain not less than 0.25 mg. of nitric oxide. The method has an accuracy and precision of 99.0 percent.

#### 1946

BATES, D. R., AND MASSEY, H. S. W., "The Basic Reactions in the Upper Atmosphere. I," *Proc. Roy. Soc. (London)* A 187, 261 (1946).

In this paper the authors discuss the fundamental processes that might be involved in the properties of the upper atmosphere, the ionosphere and the night sky emission. It is stated that various diatomic compounds of oxygen and nitrogen might be expected to occur in the upper atmosphere.

Band emissions arising from nitric oxide have been reported in the night sky spectrum. The authors state that there is evidence of the emission of the Schumann-Runge bands ( $B^2\Sigma \rightarrow X^2\Sigma$ ) of  $\text{O}_2$ , and possibly the  $\beta$  ( $B^2\Pi \rightarrow X^2\Pi$ ) and  $\gamma$  ( $A^2\Sigma \rightarrow X^2\Pi$ ) bands of NO. There are a number of unidentified bands a rather strong one at  $\lambda$  3556 Å.

WOOLLEY, R. V. D. R., "The Mechanism of Ionospheric Ionization," *Proc. Roy. Soc. (London)* A 187, 414 (1946).

In this paper the author discusses available mechanisms for the production of electrons in the E,  $F_1$  and  $F_2$  regions of the ionosphere. Among other sources of electrons in the  $F_1$  layer, nitric oxide is briefly discussed.

The first ionization potential of nitric oxide is 9.1 V, but the ionization continuum has not been observed by Price (1943). The examination of the  $\text{N}_2$  absorption spectrum with high dispersion by Worley and Jenkins (*Phys. Rev.* 54, 304 (1938)) revealed an ionization continuum at the first ionization potential which was at one time thought not to exist, or according to Price and Collins (*Phys. Rev.* 48, 714 (1935)) thought to be very weak.

It may be supposed that higher dispersion may reveal a continuum for NO. A single band in the spectrum of NO has been observed by Duffieux and Grillet (*Compt. rend.* 202, 937 (1936); 205, 39 (1937)). The band head is at 5999 Å. If this band is a transition to the ground state, the second ionization potential of NO is at 11.2 V.

Nitric oxide would be distributed exponentially with height in an isothermal atmosphere in which there is no change in the intensity of photodissociating radiation. The concentration of NO in the actual atmosphere will accordingly be on an exponential curve at great heights at which both  $O_2$  and  $N_2$  are highly dissociated. The population of NO will fall off from this curve at just that point where absorption of the radiation which dissociates  $N_2$  begins to be appreciable. This may be expected to occur at about the altitude of the  $F_1$  region.

## 1947

BATES, D. R., AND MASSEY, H. S. W., "The Basic Reactions in the Upper Atmosphere. II. The Theory of Recombination in the Ionized Layers," *Proc. Roy. Soc. (London)* A 192, 1 (1947).

In discussing the dissociation of molecular nitrogen, the effect dissociative recombination would have in producing atomic nitrogen is considered. This is probably difficult to achieve by the direct action of radiation.

The mean rate of formation of nitrogen atoms in the region of the upper layers may be of the order of 10 to 100 cc. sec. The formation of molecular nitrogen is mainly by a three-body process, the coefficient for this process is unlikely to be greater than  $10^{-31}$  cm<sup>5</sup> sec. Since the total particle density is only of the order of  $10^{10}$  to  $10^{11}$  at these altitudes, equilibrium nitrogen molecules would be almost completely absent.

This effect, the authors state, may have to be taken into consideration in the study of the formation of oxides of nitrogen. The most frequent collision a nitrogen atom is likely to encounter is one involving an oxygen atom which would lead to the formation of nitric oxide. Nitric oxide, which is not readily destroyed, may be an important constituent of the upper atmosphere. Elvey, Swings and Linke (*Astrophys. J.* 93, 337 (1941)), and Price (*Reports Prog. Phys.* 9, 10 (1942-43)) have discussed evidence for the presence of nitric oxide in the upper atmosphere.

## 1948

GILBERT, NATHAN, AND DANIELS, FARRINGTON, "Fixation of Atmospheric Nitrogen in a Gas Heated Furnace," *Ind. Eng. Chem.* 40, 1719-23 (1948).

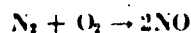
Nitric oxide is produced by heating air above 2000°C and chilling it very quickly. In the following table

Equilibrium Concentration of Nitric Oxide in Air

Temperature deg. K	$K_p$ atmos $\times 10^4$	Volume percent NO		
		20% $O_2$	10% $O_2$	5% $O_2$
1800	1.21	0.44	0.31	0.22
1900	2.31	0.61	0.43	0.31
2000	4.08	0.81	0.57	0.40
2100	6.86	1.05	0.74	0.53
2200	11.00	1.33	0.94	0.67
2300	16.90	1.64	1.16	0.82
2400	25.10	2.00	1.42	1.00
2500	36.00	2.40	1.70	1.20
2600	50.30	2.84	2.01	1.42
2700	68.70	3.32	2.34	1.66



the equilibrium concentrations of nitric oxide in air are given. For the reaction,



the equilibrium constant,  $K_p$ ,

$$\frac{P_{\text{NO}}^2}{P_{\text{N}_2} + P_{\text{O}_2}}$$

has been calculated accurately from spectroscopic data by Giauque, W. F. and Clayton, J. O. (*J. Am. Chem. Soc.* 54, 1731 (1932)).

GLOCKER, C., "The Heat of Dissociation of Nitric Oxide," *J. Chem. Phys.* 16, 604 (1948).

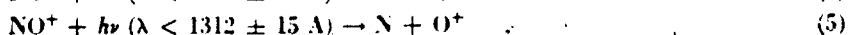
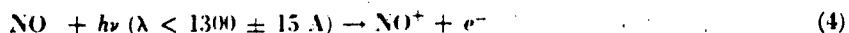
In this study of the heat of dissociation of nitric oxide, the author gives the value 6.49 ev on the basis of comparison of the series CO, NO, O<sub>2</sub>, OF, its band spectrum and the photochemical dissociation of nitric oxide.

NICOLET, M., "Deductions Regarding the State of the High Atmosphere. The Emission Spectra of the Night Sky and Aurorae," *Phys. Soc. (London)*, pp. 36-48 (1948).

In a paper read at the International Conference on "The Emission Spectra of the Night Sky and Aurorae" held under the auspices of the Gassiot Committee of the Royal Society in London July 1947, Nicolet gave a discussion of the principal processes resulting from photodissociation and photoionization. The following reaction mechanisms were given for nitric oxide.



From the above reactions the conclusions were that in the presence of atomic oxygen, NO is formed. The NO molecule is photoionized by the following processes.



NO and O<sub>2</sub> are considered to characterize the atmospheric range of the E region. The author states that if the absorption coefficient for the photoionization of O<sub>2</sub> is higher than the coefficient for the photodissociation the E layer is formed under the influence of photo-spheric radiation

$$1000 \geq \lambda \leq 910 \text{ \AA. NO is ionized by the radiation}$$

$$1300 \geq \lambda \leq 1000 \text{ \AA below the E layer.}$$

#### 1949

DURAND, E., OBERLY, J. J., AND TOUSEY, R., "Analysis of the First Rocket Ultraviolet Solar Spectra," *Astrophys. J.* 109, 1-16 (1949).

In this paper the solar spectra from V-2 flights on 10 October 1946, and 7 March 1947 are analyzed. The spectral region from 2900 Å to 2200 Å hitherto unobserved was found to be intensely complex. The structure between 2200 Å and 2300 Å, the authors state, could not be interpreted in terms of atomic lines and may be caused by atmospheric bands of NO.

Reference is made to the work of Leifson (*Astrophys. J.* 63, 73 (1926)) who showed that a layer of NO only 0.5 mm thick at N. T. P. produces appreciable absorption in the strong band centered at 2264 Å. The

authors state that although it was not the purpose of their paper to analyze the possible band spectra, the band of NO centered at 2264 Å does exist. In Figure 4C in the paper densitometer tracings of the solar spectrum taken at 55 km 10 October 1946 are shown. At this altitude the residual atmosphere above the spectrograph was equivalent to about 5 meters of air at N. T. P. An average concentration of only 0.01 percent of NO in the outer atmosphere would be detectable.

MASSEY, H. S. W., HOYLE, F., LOVELL, A. C. B., FINDLAY, J. W., ET AL., "Ionization in the Earth's Upper Atmosphere. A Geophysical Discussion. University of Manchester, England, 2 July 1949," *Observatory* 69, 185 (1949).

In this geophysical discussion of the ionization in the earth's upper atmosphere it is stated that the D layer, attributed to the ionization of nitric oxide



is not as easily explained as the formation of the F<sub>1</sub> layer which was considered to be due to the photoionization of atomic oxygen. With respect to nitric oxide it was considered very unlikely that radiation energy greater than 7 ev could penetrate to the depth of the D layer which would be necessary to photoionize NO at this level.

NICOLET, M., "Le Probleme des Regions Ionospherique," "The Problem of the Regions of the Ionosphere," *J. Geophys. Research* 54, 373 (1949).

The effects upon O<sub>3</sub>, O<sub>2</sub>, O, Na, H<sub>2</sub>O vapor, N<sub>2</sub>, N, NO and He are discussed. Since it is impossible to determine a priori the vertical distribution of the neutral constituents in relation to temperature which is not well-known, we must none the less recognize the role of the photodissociation of O<sub>2</sub>, the maximum of which is accompanied by a maximum concentration of O at about 105-110 km in the middle latitudes. The presence of the nitrogen atom in the upper atmosphere is beyond doubt, since its forbidden transitions are observed in the polar aurorae as well as in the aurorae of the lower latitudes.

From processes of recombination occurring in the region of O<sub>2</sub> dissociation one may infer the formation of NO which may play some role in the absorption of solar radiation. It should be remembered that even with atomic nitrogen present molecular nitrogen does not undergo such complete dissociation as O<sub>2</sub> because N<sub>2</sub> bands are observed up to the highest altitudes.

The upper atmosphere begins with photodissociation of molecular oxygen which is accompanied by the dissociation of N<sub>2</sub> and the formation of NO.

1950

BATES, D. R., AND NICOLET, MARCEL, "Absorption Cross-Sections," *J. Geophys. Research* 55, 306 (1950).

With reference to nitric oxide the authors state that although the amount of nitric oxide in the atmosphere is unknown, it is probably present. The evidence for this is that NO is one of the photodissociation products of N<sub>2</sub>O. The latter is a known constituent of the atmosphere and is probably more abundant than ozone. No determination of the associated cross-section for NO has been made. It is stated that there is insufficient data to calculate the attenuation. However, it was thought to be unimportant since solar radiation has been found from rocket experiments to penetrate to at least the 70-km level.

BATES, D. R., AND SEATON, M. J., "Theoretical Considerations Regarding the Formation of the Ionized Layers," *Proc. Phys. Soc. (London)* **63 B**, 129. (1950).

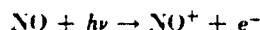
In addition to other mechanisms involved in the formation of the E, F<sub>1</sub>, F<sub>2</sub> and D layers by solar ultra-violet radiation, the photoionization of nitric oxide (NO) is discussed. The authors state that it is not unlikely that nitric oxide is an important constituent of the upper atmosphere.

As evidence for this, reference is made to reports by Price, and by Sutherland and Callendar (*Reports Prog. Phys.* **9**, 10, 18 (1942-43)). There is also reason to believe that atomic nitrogen along with atomic oxygen occurs in the upper atmosphere. Nitric oxide would be formed by chemical action. The work of Durand, Oberly and Tousey (*Astrophys. J.* **109**, 1 (1949)) is also cited as possibly direct confirmatory evidence of the occurrence of nitric oxide in the upper atmosphere. These investigators observed in the spectrum of the sun taken during a rocket flight to a height of 55 km a broad band lying between  $\lambda$  2200 Å and  $\lambda$  2300 Å. They suggested that it might be caused by absorption by atmospheric nitric oxide. If this interpretation should prove to be correct the number of NO molecules above the 55 km level must be of the order  $10^{14}$  cm<sup>2</sup> column.

The authors state that lack of data makes it impossible to investigate the photoionization of nitric oxide sufficiently quantitatively to establish if it is responsible for the formation of the D layer. In considering the possibility, the following assumptions and conclusions are given.

(1) Consistent with a total NO content of  $10^{14}$  cm<sup>2</sup> column the authors take  $n(\text{NO})_{75\text{km}}$  to be  $2 \times 10^{11}$ /cm<sup>3</sup> and  $n(\text{NO})_{90\text{km}}$  to be  $4 \times 10^{10}$ /cm<sup>3</sup>.

(2) The cross-section for the process



is low according to Price (1942-43). The authors arbitrarily adopt a value of  $5 \times 10^{-20}$  cm<sup>2</sup>.

(3) A temperature of 6000°K for black body radiation is adopted.

From the work of Preston (*Phys. Rev.* **57**, 887 (1940)) and of Hopfield (*Astrophys. J.* **104**, 208 (1946)) the atmosphere is treated as opaque except for two groups of windows: (a) in one, containing L<sub>α</sub> and of 5 Å width, the absorption cross section is about  $2 \times 10^{-21}$  cm<sup>2</sup>, (b) in the other, 20 Å width, the absorption cross section is  $5 \times 10^{-21}$  cm<sup>2</sup>. This gives a photon flux at 75 km as about  $1 \times 10^9$  cm<sup>2</sup> sec and that at 90 km about  $2 \times 10^{10}$  cm<sup>2</sup> sec.

Combining (1), (2) and (3)

$$n(\text{NO})_{75\text{km}} \approx 10 \text{ /cm}^2\text{/sec}$$

$$n(\text{NO})_{90\text{km}} \approx 40 \text{ /cm}^2\text{/sec}$$

Since these rates are considerable, it may be that the photoionization of nitric oxide actually does yield the major part of the ordinary D layer.

BENITEZ, L. E., AND PENNER, S. S., "The Emission of Radiation from Nitric Oxide. Approximate Calculations," *J. Applied Phys.* **21**, 907 (1950).

Nitric oxide at elevated temperatures is encountered in many solid-fuel and liquid-fuel rocket motors. Because of this the determination of emissivity of nitric oxide as a function of temperature was studied.

Nitric oxide is one of the diatomic molecules which may contribute to radiant heat transfer in high pressure combustion chambers. Emissivity calculations for nitric oxide at temperatures from 300° K to 3000° K were carried out.

In Tables I and II in the paper the results of effective band-widths for the fundamental and the first overtone of NO as a function of temperature are listed for two different values of  $j_{\max}$  at each temperature. From the data in these tables the limiting emissivities were calculated.

FEAST, M. W., "Two New  $\Sigma - \Sigma$  Systems due to the Molecule NO," *Can. J. Research* 28 A, 488 (1950).

In this paper the author has reported his experiments on the emission band system at 6000 Å found in discharges in flowing NO<sub>2</sub> and attributed to NO by Jausserant, Grillet, and Duffieux (*Compt. rend.* 205, 39 (1937)). The experimental arrangements and appearance of the spectra in the discharge tube are given.

The analysis of the 6000 Å band system and the analysis of the 11,000 Å band system of NO are discussed. The 11,000 Å band was photographed in the first order of the 21-foot grating (2.64 Å mm at 11,000 Å) and measured against Fe arc lines in the overlapping third order.

The emission band system at 6000 Å was shown to be due to  $E \Sigma^+ \rightarrow A \Sigma^+$  (a new level) (the upper state of the  $\gamma$  system) of the NO molecule. The band system at 11,000 Å corresponding to the transition  $D \Sigma^+ \rightarrow A \Sigma^+$  (upper state of the  $\epsilon$  system of NO) was also observed.

#### 1951

BATES, D. R., "The Temperature of the Upper Atmosphere," *Proc. Phys. Soc. (London)* 64 B, 805 (1951).

In this paper Bates considers the heat gain and heat loss processes in order to determine if the high temperature of the atmosphere in the F regions is consistent with currently accepted theories on the ionosphere. Thermal equilibrium in the F layers, rate at which energy is gained from ionizing photons, and various loss processes are examined.

Conduction and probably emission by the magnetic dipole connecting the two low levels of the ground term of atomic oxygen are found most effective. The energy source however appears inadequate to maintain the high temperature in the upper atmosphere. Sufficient energy might be supplied either by band absorption by nitric oxide, or by incoming interstellar matter both of which does not appear attractive.

In respect to polyatomic molecules which are considered to be extremely rare at great altitudes owing to photodissociation, emission from carbon monoxide (CO) and nitric oxide (NO) is discussed. If there is a Boltzmann distribution among the vibrational levels of a constituent X, the rate of radiation of energy in the  $1 \rightarrow 0$  transition is given by the following expression:

$$R^V(X) = f(X) N \epsilon_1^V \exp(-\epsilon_1^V/kT) A_{1-0}^V$$

where  $f(X)$  is the fractional concentration of the constituent,  $\epsilon_1^V$  is the excitation energy and  $A_{1-0}^V$  is the Einstein coefficient.

The Einstein coefficient for a vibrational transition in a molecule composed of atoms of different nuclear charge is usually high, and as a result the emission of such substances as carbon monoxide and nitric oxide may be significant.

The rate of population of the first vibrational level by inelastic collisions is considered. This rate is expressed by  $f(X) N^2 K \exp(-\epsilon_1^V/kT)$  where  $K \exp(-\epsilon_1^V/kT)$  is the coefficient associated with

the excitation mechanism, X is CO or NO. For CO  $\epsilon_1^V$  is 0.27 ev and for NO  $\epsilon_1^V$  is 0.23 ev (Herzberg (1950) "Molecular Spectra and Molecular Structure — Diatomic Molecules," 2d Ed., N. Y., D. Van Nostrand). The emission rate,  $R^V(X)$  can be taken to be the same. When the temperature is 1500° K it may be seen that for either substance  $R^V(X) R^E(O) \approx 2 \times 10^3 f(X) \text{ NK}$ . Since it is very difficult to convert translational energy into vibrational energy, the value of K is extremely low. A value of  $10^{-14} \text{ cm}^3/\text{sec}$  which corresponds to an efficiency of about  $2 \times 10^{-5}$  collision can be adopted without serious under-estimation.  $R^V(X) R^E(O) \approx 6 \times 10^2 f(X) R^E(O)$  is the net rate at which energy is lost.

The carbon monoxide in the upper atmosphere results from the photodissociation of carbon dioxide. Near ground level  $f(\text{CO}_2)$  according to Paneth (1937) is  $3 \times 10^{-4}$ . As  $f(\text{CO})$  can scarcely exceed this,  $R^V(\text{CO}) R^E(O)$  must be small. In the absence of evidence to the contrary it seems best to assume that nitric oxide is a very minor constituent in the atmosphere at all altitudes. Thus  $R^V(\text{NO}) R^E(O)$  is also less than unity.

BROWNS, G. M., "The Airglow," *Sci. Progress* 39, 623 (1951).

With reference to the presence of the emission spectrum of nitric oxide (NO) the author states that the  $\beta$ -band of NO in the ultraviolet region with the following emission process



and the  $\gamma$ -band of NO in the ultraviolet with the emission process



are possibly present.

Reference is made to Bates and Seaton (1950) for evidence that NO is an important constituent of the upper atmosphere. The following recombination processes are considered.



The author states that the dissociation energies  $D(\text{N}_2)$  and  $D(\text{NO})$  are not known unambiguously. However, Herzberg and Sponer (1934) gave the value 7.38 ev. for  $D(\text{N}_2)$ , and Herzberg (1939) gave the value 5.3 ev for  $D(\text{NO})$ . Gaydon and Penny (1944) have given 9.76 ev for  $D(\text{N}_2)$  and 6.49 ev for  $D(\text{NO})$ .

HERZBERG, G., "The Atmospheres of the Planets," *J. Roy. Astron. Soc. (Canada)* 45, 100 (1951).

A review of the present status of spectroscopic investigations of the earth and terrestrial planets is given in the present paper by Herzberg. Much new information about the earth's atmosphere has been derived from a study of its absorption spectrum. It has been found that the spectrum of any celestial object breaks off rather abruptly at about 3000 Å, while the spectrum of a distant light source on the surface of the earth does not break off in a similar manner.

The cause of this break-off is now known to be due to the absorption of the ozone layer which exists at an average height of 25 km. In the laboratory the ozone absorption becomes negligible at about 2200 Å. However, in the earth's atmosphere no light transmission below 2200 Å is observed. The author gives as a reason for this additional absorption as probably the continuum joining on a weak ultraviolet band system of  $\text{O}_2$  which was discovered by Herzberg (*Naturwiss.* 20, 577 (1932)).

Reference is made to the solar spectrum studies from V-2 rockets at great heights above the ozone layer. The spectrum was found under these conditions to extend to about 2200 Å where it seems to be sharply limited. The O<sub>2</sub> absorption would have little effect at the altitudes reached by rockets. Since there is a discrete absorption due to the NO molecule which under the low dispersion employed in these experiments, the author suggests that this apparent cut-off at 2200 Å may be due to NO if there is sufficient amount present in the upper atmosphere.

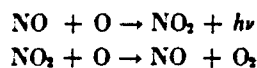
JOHNSTON, HAROLD S., AND PERRINE, RICHARD L., "Decomposition of Nitrogen Pentoxide in the Presence of Nitric Oxide. II. Details at Low Pressures," *J. Am. Chem. Soc.* 73, 4782 (1951).

The authors have reported their studies on the decomposition of nitrogen pentoxide in the presence of nitric oxide. The experiments employed a 22-liter flask at pressures from 0.05 to 10 mm Hg, and at three temperatures 27.0, 50.1 and 71.3°C.

The results were analyzed in terms of collisional theories of the low-concentration limit for unimolecular reactions. By comparison of their results with those of Hodges and Linhorst (*J. Am. Chem. Soc.* 56, 836 (1934)) who used pure nitrogen pentoxide, the authors state that the second-order rate of activation at low concentration becomes the same for the two systems.

KRASOVSKII, V. I., "Influence of Water Vapor and Oxides of Carbon and Nitrogen on the Luminescence of the Night Sky," *Doklady Akad. Nauk. SSSR* 78, 669 (1951).

Among other mechanisms the following involving nitric oxide are given.



KRASOVSKII, V. I., AND LUKASHENYA, V. T., "Interpretation of the 10,000 Å Region of the Night Sky Spectrum," *Doklady Akad. Nauk. SSSR* 80, 735 (1951).

The authors state that bands in the 9,700-10,300 Å region previously considered to be due to OH molecules may possibly be due to NH molecules. The primary excitation was thought to involve ternary collisions which yielded excited molecules of O<sub>2</sub>, N<sub>2</sub>, O<sub>3</sub>, NO, and N<sub>2</sub>O.

MITRA, A. P., "The D-Layer of the Ionosphere," *J. Geophys. Research* 56, 373 (1951).

In this paper which discusses the D-layer of the ionosphere the author refers to Nicolet ("Mixed Commission on Ionosphere," U. R. S. I. Bruxelles, p. 50 (1948)) who considered that there are three elements operative in the formation of the D-region. They are:

- (a) The normal layer by ionization of O<sub>2</sub> at its first ionization potential 12.2 ev.
- (b) A layer more or less sporadic by ionization of sodium.
- (c) A layer of extra ionization of NO by radiation at λ 1300 Å (during fade-out). The possibility of radio fade-out (the Mogel-Dellinger effect) enhancement by NO is briefly discussed.

SWINGS, P., "Spectroscopic Problems of Astronomical Interest," *J. Opt. Soc. Am.* 41, 153 (1951).

In a brief discussion of the atmosphere of the Earth the author mentions the numerous emissions in the ultraviolet and photographic regions which have been assigned to the Vegard-Kaplan system of N<sub>2</sub> and to

the Herzberg system of  $O_2$ . Both systems are forbidden transitions. The following emissions are among those yet unidentified: 3263 (5), 3571 (7), 3622 (5), 3700 (6), 3916 (8), and 3960 Å (4). The author raises the question as to whether these do not belong to the forbidden  $^4\Pi \rightarrow ^2\Pi$  intercombination of NO. In a private communication to the author Herzberg made this suggestion.

TANAKA, Y., SEYA, M., AND MORI, K., "Absorption Spectra of Nitric Oxide in the Extreme Ultraviolet," *Science of Light (Japan)* 1, No. 2, 80 (1951).

The authors report the analysis of the absorption spectra of NO in the extreme ultraviolet. Vacuum spectrographs with 1- and 3-meter concave gratings respectively were employed. Six new band progressions were found. The dissociation energy of the upper state of the  $\gamma$ -bands was shown by calculation to have values much lower than those formerly accepted.

TANAKA, Y., AND SAI, T., "Emission Bands of Nitric Oxide in the Extreme Ultraviolet Region," *Science of Light (Japan)* 1, No. 2, 85 (1951).

The emission spectrum of NO was photographed in the spectral region from 2200 Å to 1450 Å. The  $\gamma$  system and the  $\epsilon$  system could be distinguished. They were compared with the absorption spectra. The band systems were named A, B, C, D and E. The authors concluded that these are caused by the transition from the newly discovered excited electronic states to the ground state.

VEGARD, L., AND G. KVIETE, "An Auroral Spectrogram and the Results Derived From It," *Geofys. Publikasjoner, Norske Videnskaps-Akad.*, Oslo 18, No. 3 (1951).

This is a report of the observations of a brilliant auroral display during the night of 23-24 February 1950 at Oslo. The spectrograph employed was a new one and compared with the best spectrographs previously used in Norway, the dispersion was about twice as large and the light power more than five times greater. Within the region  $\lambda\lambda$  6300-3880 Å of the spectrogram about 114 lines and bands were distinct and could be measured directly from the original plate, about 50 of these were not previously observed. A great number of lines observed on the spectrogram were too weak to be measured directly from the plate. Their wavelengths were determined by means of photometer curves of great magnification.

Among other new lines and bands on the spectrogram of the auroral luminescence the following  $\beta$ -bands from NO were observed. Since in most cases these new bands nearly coincide with lines and bands which are known to be present in the auroral luminescence, their existence cannot be considered as proved. The authors point that their observations give possible evidence for the existence of these lines and bands of these constituents in the auroral luminescence. The following  $\beta$ -bands of NO are reported:

Plate $\lambda_p$	Photometer $\lambda_r$	Identification
5253.8	5256	$NO_\beta$ (3-18)
	4913	$NO_\beta$ (3-17)
	4030	$NO_\beta$ (0-12)
	3961	$NO_\beta$ (2-13)
	3880.5	$NO_\beta$ (1-12)

The two numbers in the parentheses give the vibrational quantum numbers of the upper and lower electronic state respectively.

WHITNACK, G. C., HOLFORD, C. J., GANTZ, E. ST. CLAIR, AND SMITH, G. B. L., "Determination of Nitric Oxide and Nitrogen Tetroxide in Admixture," *Anal. Chem.* 23, 464 (1951).

A precise procedure for the determination of nitric oxide and nitrogen tetroxide, and their admixtures is described. The procedure is based upon the principle of absorption of nitric oxide and nitrogen dioxide in 95 percent sulfuric acid.

Nitric acid and nitrosyl sulfuric acid are formed. The total nitrogen in the solution is determined by means of a nitrometer. Nitrosyl nitrogen is determined by titration with a solution of potassium permanganate.

A description of materials and apparatus is included in the paper. The procedure and method of calculations are given in detail.

#### 1952

BAER, P., AND MIESCHER, E., "Band Spectra in the Schumann Region of  $\text{N}^{15}\text{O}$  and  $\text{N}_2$  with Enriched Nitrogen-15," *Nature* 169, 581 (1952).

The emission spectra of  $\text{N}^{15}\text{O}$  were photographed in connection with the investigation of a new band system of the NO molecule ( $\beta' - X' \pi$ ). The following topics are discussed: (1) NO (a)  $\epsilon$ -bands and (b)  $\beta'$ -bands; (2)  $\text{N}_2$ , and (3) the New System found by the authors. In Table 3 in the paper the wave-numbers of the heads of the new isotope band are shown. A provisional analysis is made. The  $\epsilon$ -bands for NO definitely belong to a new system.

BATES, D. R., "Some Reactions Occurring in the Earth's Upper Atmosphere," *Ann. geophys.* 3, 194 (1952).

At the 90 and 75 km levels respectively  $n(\text{N}_2)$  is approximately  $7 \times 10^{13}$  and  $8 \times 10^{14}/\text{cm}^3$ . Durand, Oberly and Tousey (*Astrophys. J.* 109, 1 (1949)) observed certain features in the spectrum of the sun at an altitude of 55 km. The region between  $\lambda$  2200 and 2300 Å gave evidence of absorption by atmospheric nitric oxide.

If this interpretation should prove to be correct from experimental work by Leifson (1926) the number of NO molecules above the 55 km level would be of the order of  $10^{18}/\text{cm}^2$  column.

The only other spectroscopic evidence is that by Nicolet (*Phys. Soc. (London)*, p. 105 (1948)). Nicolet called attention to striking coincidences between some of the auroral emissions and members of the  $\beta$ -band system.

Moses and Wu (*Phys. Rev.* 83, 109 (1951)) and Bates and Seaton (*Proc. Phys. Soc.* 63 B, 129 (1950)) have suggested the following process to be responsible for the formation of the D layer.



The author states that if atomic nitrogen and nitric oxide are constituents of the upper atmosphere, nitrogen peroxide ( $\text{NO}_2$ ) should also exist. Price (*Reports Prog. Phys. (London)* 9, 10 (1942-43)) has pointed out that the number of molecules of  $\text{NO}_2$  present during the day must be less than  $3 \times 10^{17}/\text{cm}^2$  column, or the characteristic absorption bands would be observed in the solar spectra. There does not seem to be any direct positive evidence on the occurrence of  $\text{NO}_2$  in the upper atmosphere.



MAYENCE, J., "Absorption Spectra at Low Temperature. Study of  $N_2O$  gas, NO gas and liquid," *Ann. Phys.* (Paris) 7, 453-505 (1952).

In this report on the absorption of nitric oxide there were no absorption peaks of NO in the spectral region 4000-8500 Å. Within the range 2267-1549 Å vibrational peaks are listed. There are continuous bands with peaks at  $\lambda$  1820 Å and  $\lambda$  1470 Å.

NICOLET, M., AND MANGE, P., "An Introduction to the Study of the Physical Constitution and Chemical Composition of the High Atmosphere," Ionospheric Research, Scientific Report No. 35, State College, Pennsylvania, April 15, 1952, Contract No. AF 19(122)-44.

In this extensive study of the vertical distribution of molecular and atomic oxygen, the authors state in the conclusions that below the E layer, photoionization processes depend strongly on the absorption coefficient of molecular oxygen in the spectral region 1020-900 Å.

The NO molecule, which is able to absorb the Lyman-alpha radiation, is, stated by the authors, an important constituent in the D region. The rocket results and the photochemical investigations discussed in this report seem to support this origin of the D region. Evidence for this is the existence of atomic oxygen and the recombination of atomic nitrogen at heights below 100 km which leads to the formation of NO.

VEGARD, L., AND E. TÖNSBERG, "Results from Auroral Spectrograms obtained at Tromsø during the Winter of 1950-51," *Geofys. Publikasjoner, Norske Videnskaps-Akad.*, Oslo 18, No. 8 (1952).

During the summer of 1950 the new spectrograph used by Vegard and Kvifte (1951) during the night of 23-24 February 1950 was moved to the Auroral Observatory at Tromsø. The plan in the present work was among others to obtain strongly exposed spectrograms from which a great number of the weak lines could be accurately measured so as to check the wavelengths of the values previously obtained from the spectrogram taken at Oslo 23-24 February 1950.

The measurements of the  $\beta$ -bands of NO from the spectrogram obtained at Tromsø of the auroral luminescence are reported as follows:

Oslo ( $\lambda_r$ )	Tromsø ( $\lambda_r$ )	Identification
5256	5255.4	$NO\beta$ (3-18)
4913	—	$NO\beta$ (3-17)
4030	4029.5	$NO\beta$ (0-12)
3961	—	$NO\beta$ (2-13)
3880.5	—	$NO\beta$ (1-12)

The two numbers in the parentheses give the vibrational quantum numbers of the upper and lower electronic state respectively.  $\lambda_p$  values were measured directly from the plate.  $\lambda_r$  values were obtained from the photometer curve.

VIRTANEN, ARTTURI I., "Molecular Nitrogen Fixation and Nitrogen Cycle in Nature," *Tellus* 4, 304 (1952).

In the present paper the author discusses the origin of nitrogen oxides in the atmosphere, and states that  $N_2$ -fixation in the atmosphere is possibly photochemical. The ozonosphere, at altitudes higher than 10 km, is considered to have, probably, conditions favorable for this fixation. It is suggested that ozone oxidizes the nitrogen oxide formed to nitrogen pentoxide, the latter having been reported by Adel and Lampland

(1938). It is further suggested that there may be a downward movement of nitrogen pentoxide by means of rain, while the rising nitrogen pentoxide is decomposed by photochemical dissociation. The observations of Elvey (1942) on the spectral bands of nitric oxide (NO) at altitudes 90-140 km are cited as evidence for this mechanism.

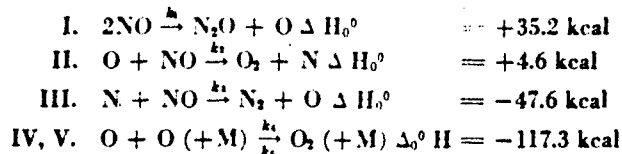
The possibility of the formation of nitrate nitrogen by the atmospheric oxidation of nitrous oxide is also considered. The nitrous oxide ( $N_2O$ ) originating from the soil, is decomposed photochemically into  $N_2$ ,  $O_2$ , and NO by radiation of wavelength  $\lambda < 2000 \text{ \AA}$  in the upper atmosphere. Nitric oxide (NO) is further dissociated into  $N_2$  and  $O_2$ , and may also be oxidized to nitrogen dioxide ( $NO_2$ ) during its transport from high altitudes to lower atmospheric levels. Consequently nitrous oxide may be a source of a part of the nitrate nitrogen.

The author expresses the opinion that the analyses of the precipitation do not give full information concerning the origin, and possible participation of oxides of nitrogen in the chemical reactions in the atmosphere. There is also needed more quantitative data about the different nitrogen compounds present in all levels of the atmosphere. This should elucidate the nitrogen cycle in nature.

WISE, HENRY, AND FRENCH, MAURICE F., "Kinetics of Decomposition of Nitric Oxide at Elevated Temperatures. II. The Effect of Reaction Products and the Mechanism of Decomposition," *J. Chem. Phys.* 20, 1724 (1952).

This is an extension of the author's studies on the kinetics of decomposition of nitric oxide. In the first paper of the series (*J. Chem. Phys.* 20, 22 (1952)) the authors report the results of their investigations in using a quartz vessel. Below  $1000^\circ \text{K}$  the decomposition of nitric oxide was shown to be of a heterogeneous mechanism, and of a homogeneous mechanism above  $1600^\circ \text{K}$ .

In the present paper the effects of nitrogen and oxygen on the kinetics of decomposition of nitric oxide were investigated. The apparatus and experimental procedures were similar to those reported in the first paper of the series. Based upon the experimental results the authors give the following mechanism of thermal decomposition of nitric oxide.



The temperature range was from  $980^\circ \text{K}$  to  $1912^\circ \text{K}$ . The research was carried out at the Jet Propulsion Laboratory, California Institute of Technology under Contract No. DA-04-495-ODR 18 sponsored by the Department of the Army Ordnance Corps.

1953

BAER, P., AND MIESCHER, E., "NO, NO and N<sub>2</sub> Emission Spectra in the Schumann Region," *Helv. phys. Acta* 26, 91-110 (1953).

The authors report a new band system ( $\beta'$ ) of the NO molecule in the region 2000 - 1500 Å which forms a  $B'(\Sigma) - X^2\Pi$  transition. Bands in the visible region were interpreted as  $B'(\Sigma) - B^2\Pi$  system of NO. The isotope shifts observed in the  $\gamma$  and  $\epsilon$  bands of the NO molecule definitely show that these bands form two separate systems. A new band  $A^1\Pi - X^2\Sigma$  of the NO<sup>+</sup> ion was found between 1700 and 1350 Å.

Two figures of emission band spectra from 2100-1600 Å, and from 1600-1350 Å are shown with explanations. A bibliography of 25 references is included.

BYRAM, E. T., CHUBB, T., FRIEDMAN, H., AND GAILAR, N., "Lyman-Alpha Radiation in the Solar Spectrum," *Phys. Rev.* 91, 1278 (1953).

In this letter to the editor these scientists from the U. S. Naval Research Laboratory report that the intensity of the Lyman-alpha line of hydrogen ( $\lambda$  1216 Å) in the solar spectrum was measured by means of photon counters flown in three Aerobee rockets. A continuous telemetered record of the intensity versus altitude up to about 128 kilometers was obtained.

Lyman-alpha radiation of hydrogen was first detected at about  $74 \pm 2$  km ( $18^\circ$  -  $20^\circ$  sun elevation) altitude in each of the three flights. The measured solar intensity reported in this letter is  $0.10 \pm 0.02$  erg cm<sup>-2</sup> sec<sup>-1</sup> at the top of the atmosphere which is lower than  $0.4$  erg cm<sup>-2</sup> sec<sup>-1</sup> the result reported by Tousey, Watanabe and Purcell (*Phys. Rev.* 83, 792 (1951)).

Reference is made to Hopfield's spectrogram (*Astrophys. J.* 104, 208 (1946)) which showed the existence of a deep window in the O<sub>2</sub> absorption spectrum at Lyman-alpha, and also to the quantitative measurements by Watanabe, Marmo and Inn (*Phys. Rev.* 90, 155 (1953)) of the absorption coefficients in the neighborhood of this window.

The suggestion by Bates and Seaton (*Proc. Phys. Soc. (London)* 63 B, 129 (1950)), and by Nicolet (*Mem. Roy. Meteorol. Inst. (Belgium)* 19, 1 (1945)) that absorption of Lyman-alpha radiation ( $H\ L_\alpha$ ) by NO may produce the observed D-layer ionization is also alluded to. The authors state that the present rocket data do not exclude this possibility. If it is assumed that the contribution of H<sub>2</sub>O or NO to the absorption observed in the rocket experiment is less than ten percent, the maximum concentration of H<sub>2</sub>O and NO relative to air must have been less than  $1.6 \times 10^{-5}$  and  $9.4 \times 10^{-5}$  respectively, using absorption coefficients 390 cm<sup>-1</sup> and 67 cm<sup>-1</sup> for H<sub>2</sub>O and NO. The latter concentration is equivalent to an upper limit of 0.007 cm (N. T. P.) of NO above 75 km which is much less than the value of 0.02 cm (N. T. P. given by Migotte and Neven (*Mem. Roy. Soc. Sci. (Liege)* 12, 165 (1952)) as the maximum possible abundance from solar infrared studies.

Reference to the work of Watanabe, Marmo and Inn (*Phys. Rev.* 90, 155 (1953)) is cited. They found that approximately 50 percent of the absorption of NO at the wavelength of  $H\ L_\alpha$  leads to photoionization. The authors of the present paper state that if only one percent of the  $H\ L_\alpha$  intensity observed in the rocket experiment were absorbed by NO, the rate of ion production in the D layer would average about 15 ion pairs cm<sup>-3</sup> sec<sup>-1</sup> which would be of the order of magnitude required to produce the D layer (Bates and Nicolet, loc. cit.).

INN, EDWARD C. Y., "The Photoionization of Molecules in the Vacuum Ultraviolet," *Phys. Rev.* 91, 1194 (1953).

A method for measuring ionization potentials of molecules in the vacuum ultraviolet is described. The apparatus employed was a Baird 1-meter Vacuum Ultraviolet Monochromator from which the radiation passed through the photoionization cell. The ions produced by photoionization were collected by use of parallel platinum electrodes placed outside of the light path within the cell. The ion current was measured with a Beckman micro-micro-ammeter ( $10^{-8}$  -  $10^{-11}$  amp.) and recorded on a Speedomax recorder.

The spectral region was scanned near the threshold. The ion current, and the wavelength that which the first ions appeared, followed by a sharp increase in the ion current were noted. In addition to the ionization potentials of various organic gaseous compounds the author lists the following values obtained of first ionization potentials for  $O_2$ , NO,  $NH_3$ , and  $SO_2$  molecules.

Molecule	Threshold Wavelength Å	1st Ionization Potential ev
$O_2$	1029	$12.04 \pm 0.01$
NO	1343	$9.23 \pm 0.02$
$NH_3$	1223	$10.13 \pm 0.02$
$SO_2$	998	$12.42 \pm 0.06$

Values previously reported in the literature by other investigators and the methods employed are also recorded in the table. The photoionization method reported in the present paper is claimed to give greater precision than by either the electron impact or the Rydberg series (spectroscopic) method. The present method (photoionization) and the Rydberg series method both give values in close agreement.

JARMAIN, W. R., FRASER, P. A., AND NICHOLLS, R. W., "Vibration Transition Probabilities of Diatomic Molecules: Collected Results  $N_2$ ,  $N_2^+$ , NO,  $O_2^+$ ," *Astrophys. J.* 118, 228 (1953).

Band systems of diatomic molecules are classified into three groups according as the results derived by approximate vibrational transitional probabilities are expected to be excellent (I), satisfactory (II), indicative trends (III).

For NO:  $A^2\Sigma^+ \rightarrow X^2\Pi$  ( $\gamma$ -bands) the classification is described as excellent. A table of  $\gamma$ -bands for NO,  $p(v', v'') = (v', v'')^2$  and a table of basic molecular constants for NO are included.

JOHNSON, F. S., PURCELL, J. D., TOUSEY, R., AND WILSON, N., "The Ultraviolet Spectrum of the Sun," Gassiot Meeting, August (1953) (Oxford, England).

In this paper presented at the Gassiot Meeting, Oxford, August 1953, the authors make reference to the suggestion made by Durand, Oberly and Tousey (*Astrophys. J.* 109, 1 (1949)) that certain features of the spectrum which they could not explain as due to solar Fraunhofer lines might be due to nitric oxide.

In the present paper the authors with the aid of more intense exposures than in 1949 have studied the existence of atmospheric nitric oxide further. Nitric oxide has a double band system near 2265 Å, and also another band system at 2150 Å. A densitometer tracing is shown of the solar spectrum. The positions of the nitric oxide band heads are shown. From this it appeared that nitric oxide is not present in sufficient quantity in either the earth's atmosphere or the sun's to cause significant absorption in this spectral region.

The conclusion is that there is no evidence for the presence of nitric oxide in either the terrestrial or solar atmosphere. Reference is also made to Migeotte and Neven (*Mem. Sor. Roy. Sci. (Liege)* 12, 165 (1952)) who were unable to find atmospheric nitric oxide from infrared studies. The latter workers concluded that no more than 0.02 cm N. T. P. of nitric oxide could be present in the earth's atmosphere.

MARMO, F. F., "Absorption Coefficients of Nitrogen Oxide in the Vacuum Ultraviolet," *J. Opt. Soc. Am.* 43, 1186 (1953).

In this paper the author has described his measurements of the absorption coefficients of nitrogen oxide (nitric oxide) in the  $\lambda$  1100-2300 Å spectral region of the ultraviolet. The method employed a photoelectric method in use at the Air Force Cambridge Research Center and described in detail by Watanabe and Inn (1953), and Watanabe, Inn, and Zelikoff (1953).

The importance of knowing the absorption spectrum in the spectral region of this study was pointed out that the formation of the D layer, according to one theory, is possibly due to the photoionization of nitrogen oxide by the solar ultraviolet between  $\lambda$  1100-1300 Å. A table is included showing some  $k$  values ( $\text{cm}^{-1}$ ) for wavelengths 1332 Å to 1514 Å for several pressures (0.52 to 100 mm Hg).

A continuous absorption spectrum was found to exist in the spectral region  $\lambda$  1100-1400 Å in which the absorption coefficients varied from 40  $\text{cm}^{-1}$  to 200  $\text{cm}^{-1}$ . At Lyman-alpha ( $\lambda$  1216 Å) the  $k$  value was 67.5  $\text{cm}^{-1}$ . Twenty-one literature references are included, as well as detailed analysis and discussion of the  $\alpha$ ,  $\delta$ ,  $\epsilon$ , and  $\gamma$  absorption bands of NO in the  $\lambda$  1500-2300 Å region.

MIESCHER, E., "Study of the Band Spectra of  $\text{N}_2^+$ , NO and  $\text{NO}^+$  in the Schumann Region with the Aid of  $\text{N}^+$ ," *Mem. Soc. Roy. Sci. (Liege)* 13, 177 (1953).

In this paper the author again reports his study of the band spectra of  $\text{N}_2^+$ , NO and  $\text{NO}^+$  with the aid of  $\text{N}^+$ . The study had previously been reported in *Helv. phys. Acta* 26, 91 (1953) and *Nature* 169, 581 (1952).

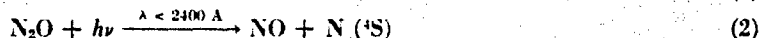
MITRA, A. P., "A Tentative Model of the Equilibrium Height Distribution of Nitric Oxide in the High Atmosphere and the Resulting D-Layer," *Ionospheric Research*, Scientific Report No. 46, The Pennsylvania State College, 15 May 1953, AMC Contract No. 19(122)-44.

In this report the author has attempted to derive a tentative model for the equilibrium distribution of nitric oxide in the 50-100 km altitude region of the upper atmosphere. The possible photochemical reactions in which ozone, both molecular and atomic nitrogen, oxygen (molecular and atomic), and nitrous oxide are considered. With reference to the D-layer formation it is stated that the absorption cross-sections of  $\text{O}_2$ , Na and NO are reliably known and also the intensity of the radiations ionizing these constituents, however information on the vertical distribution of the constituents  $\text{O}_2$ , Na and NO is lacking. It is pointed out that from the results of Moses and Wu (1952) and Nicolet and Mange (1952) and from studies of the twilight flash and night air-glow a rough model may be deduced for  $\text{O}_2$  and Na.

With reference to atmospheric NO much less is known. A review of the possible presence of NO in the upper atmosphere is given from the early evidence obtained by Durand, Oberly and Tousey (1949) from the solar spectrum during a rocket flight, and the spectroscopic evidence from the striking coincidences between auroral emissions and members of the  $\beta$ -band system discussed by Nicolet (1948). Later information from

Tousey indicated that the broad band lying between  $\lambda$  2200-2300 Å might well come from NO existing in the atmosphere of the sun.

Two possible processes for the production of NO in the upper atmosphere are given.



Certain values are obtained for height distributions of  $\text{N}_2\text{O}$ , atomic nitrogen and nitric oxide. General equations are derived for giving the distributions of N and NO. It is emphasized that these values should be considered only as preliminary and indicative of the order of magnitude of the parameters rather than absolute values. The value obtained for NO is that under the conditions of photochemical equilibrium the maximum concentration occurs within 85-95 km and does not exceed a value of about  $2 \times 10^{12} \text{ cm}^{-3}$ .

MOORE, GORDON E., WULF, OLIVER R., AND BADGER, RICHARD M., "The Photochemical Decomposition of Nitric Oxide by Absorption in the (0,0) and (1,0)  $\gamma$ -Bands," *J. Chem. Phys.* 21, 2091 (1953).

In this letter to the editor the authors describe their laboratory experiments on the photochemical decomposition of nitric oxide by absorption in the (0,0) and (1,0)  $\gamma$ -bands. This work was to check Gaydon's experiment who irradiated nitric oxide at atmospheric pressure with the light from an iron arc. Gaydon observed no evidence of decomposition of nitric oxide even after long exposures. The authors in this report used a condensed spark between cadmium electrodes because of two strong lines at 2144 and 2265 Å which overlap the (1,0) and (0,0)  $\gamma$ -bands, respectively.

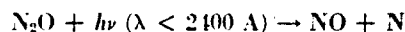
The decomposition was followed by observing the continuous absorption of  $\text{N}_2\text{O}_3$  which is formed as an end product. The experiment is of interest because of the possible connection with the heat of dissociation of nitrogen. The absorbed lines have energies of 5.77 and 5.46 eV as compared to 6.49 eV the heat of dissociation of nitric oxide as calculated from thermochemical data. The experiments are being continued in an attempt to study the mechanism of this photodecomposition of nitric oxide.

NICOLET, MARCEL, "Aeronomical Problem of Nitrogen Oxides," *Ionospheric Research*, Scientific Report No. 52, The Pennsylvania State College, 25 October 1953, AMC Contract No. AF19(122)-44.

In this report Nicolet states that nitric oxide had been considered by him (*Inst. Roy. Meteor., Belgium, Memoires* 19, 124 (1945)) to be an important constituent of the high atmosphere. From theoretical considerations the author found the possibility that NO is quite abundant below the transition region in which molecular oxygen is dissociated into atomic oxygen. Reference is made to the work of Bates and Seaton (1950), and to Watanabe, Marmo and Inn, the latter group after measuring the absorption coefficients of NO,  $\text{O}_2$  and other gases concluded that the formation of the D layer by NO could be explained since Lyman-alpha radiation is in an atmospheric window. The Lyman-alpha radiation has been observed from rocket experiments to penetrate down to 74 km by Byram, Chubb, Friedman and Lichtmen (1952).

Reference is also made to the observation made by Durand, Oberly and Tousey (1949) that the absorption band centered at 2264 Å in the solar spectrum was considered to be a band of atmospheric nitric oxide and that the abundance was about  $10^{18} \text{ molecules cm}^{-2}$  at about 55 km (Bates and Seaton, 1950). However, in a private communication to A. P. Mitra, Tousey has indicated that the band might well arise from NO existing in the atmosphere of the sun. A theoretical discussion is given of the photochemistry of the formation of nitric oxide and its vertical distribution.

The effect of nitrous oxide photodissociation,



leading to the formation of NO is also considered. Following a long theoretical discussion of nitric oxide in the solar spectrum in which the number of NO molecules near 80 km was deduced to be  $10^8$  molecules  $\text{cm}^{-3}$ , the author states that this value may be considered to be correct within one order of magnitude and as a working concentration. A discussion is also given of the importance of the reactions between nitric oxide and atomic oxygen or ozone as contributing to the day-twilight-night airglow.

HENSE, WILLIAM A., "Intensity of Lyman-Alpha Line in the Solar Spectrum," *Phys. Rev.* 91, 299 (1953).

The appearance of the Lyman-alpha line on a rocket spectrogram is described. A grazing-incident spectrograph was pointed directly at the sun during a 28-second exposure by a biaxial sun-follower in an Aerobee rocket. Lyman-alpha results from the  $1s^2S - 2p^2P$  transition in the hydrogen atom. It is actually a doublet with wavelengths 1215.668 Å and 1215.674 Å.

Reference is made to the detection of radiation between 1050 and 1250 Å by means of a thermoluminescent phosphor,  $\text{CaSO}_4:\text{Mn}$  in rockets by Tousey, Watanabe and Purcell (1951). Also solar radiation between 1180 Å and 1300 Å was detected with photon counters in rockets by Byram, Chubb, Friedman, and Lichtman (*J. Opt. Soc. Am.* 42, 876 (1952)). The radiation was not present below 74 km. From atmospheric absorption coefficients calculated from the data, the radiation was considered to be from Lyman-alpha.

In the present investigation Lyman-alpha was photographed. The spectrogram indicated that much of the 1216 Å radiation reached levels around 81 km and lower. The average virtual height of the E layer for 12 December 1952 in the White Sands region was 100 km. From this it would appear that much of the Lyman-alpha line radiation penetrated and was absorbed in the D layer.

SUN, H. AND WEISSLER, G. L., "The Absorption Coefficients of NO and  $\text{NH}_3$  in the Vacuum Ultraviolet," *Phys. Rev.* 92, 545 (1953).

This is an abstract of a paper presented at the 316th Meeting of the American Physical Society 26-30 December 1952 at the U. S. Naval Ordnance Test Station, Inyokern, and at the California Institute of Technology, Pasadena, California. The authors report their investigations of the absorption of NO between 1300 Å and 370 Å which is composed of one or more continuous regions superposed by bands.

The following absorption coefficients were observed from a plot of the coefficients  $k_\nu$  versus wavelengths: one maximum at 920 Å with  $k_\nu = 850 \text{ cm}^{-1}$ , another maximum at 620 Å with  $k_\nu = 920 \text{ cm}^{-1}$ . There were indications of small peaks at 1300 Å with  $k_\nu = 180 \text{ cm}^{-1}$  and at 760 Å with  $k_\nu = 660 \text{ cm}^{-1}$ . An absorption minimum was observed near 1200 Å with  $k_\nu \leq 50 \text{ cm}^{-1}$ . It was not possible to separate band absorption from continuous absorption.

SUTCLIFFE, L. H. AND WALSH, A. D., "The Ultraviolet Absorption Spectrum of Nitric Oxide," *Proc. Phys. Soc. (London)* 66A, 200 (1953).

The following are five well-known excited states of the NO molecule given in the order of increasing excitation: A  $^2\Sigma^+$ , B  $^2\Pi$ , C  $^2\Sigma^+$ , D  $^2\Sigma^+$ , E  $^2\Sigma^+$ . Transitions between the ground state and the first four of the above excited states give rise to the  $\gamma$ ,  $\beta$ ,  $\delta$ , and  $\epsilon$  systems respectively. Reference is made to the dis-

covery by Tanaka, Seya, and Mori (*J. Chem. Phys.* 19, 979 (1951)) of the absorption bands due to transitions between the ground state and  $E^2\Sigma^+$  states.

Reference is also made to the historic work of Leifson (1926) who first measured the absorption bands of NO in the Schumann region as far as  $\lambda$  1296 Å. The authors in the present paper report new photographs of the absorption spectrum of nitric oxide. The following topics are discussed:

- (1) The  $\beta$  System.
- (2) The  $B^2\Pi - D^2\Sigma^+$  Perturbation.
- (3) The  $\beta'$  System.
- (4) The  $B^2\Pi - C^2\Sigma^+$  Perturbation.
- (5) The  $B^2\Pi - A^2\Sigma^+$  Perturbation.
- (6) Rydberg Transitions.

An excellent bibliography of 16 references of previous investigations of the spectrum of nitric oxide is included. The authors conclude that a hypothetical repulsive curve to explain the perturbations of the various systems is unnecessary. They could be explained in terms of successive crossings of the  $^2\Sigma^+$  curves by the  $B^2\Pi$  potential curve.

TANAKA, YOSHIO, "On the Emission Bands of the NO Molecule in the Vacuum Ultraviolet Region," *J. Chem. Phys.* 21, 788 (1953).

The emission spectrum of NO in the far-ultraviolet was investigated using 85-cm and 21-foot normal incidence vacuum spectrographs. A detailed description of the experimental procedures is given.

The  $\gamma$ -bands are strongest of all the NO bands. These could be followed up to the (3,0) band on the shorter wavelength side. In the present investigation the author states that the (0,0) band appeared very strong. The heads of the (4,0)  $\gamma$ -bands come close to the heads of the (0,0)  $\epsilon$ -bands. The existence of the  $\epsilon$ -system of NO is confirmed. The author reports new bands quite similar to the  $\beta'$ -bands in the  $\lambda$  1500 Å spectral region. A tentative analysis of the  $\beta'$ -system is given.

WATANABE, K., MARMO, F., AND INN, EDWARD C. Y., "Formation of the D Layer," *Phys. Rev.* 90, 155 (1953).

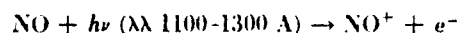
In this letter to *The Physical Review* the authors give the results of their measurements of absorption cross sections of oxygen and nitric oxide using a vacuum ultraviolet monochromator and photoelectric detection. The absorption intensity of nitric oxide with impurity less than 0.1 percent was measured in the region 1070–2300 Å. A moderately strong absorption continuum was observed in the spectral region below 1400 Å. The absorption cross section of nitric oxide at Lyman-alpha was determined to have the value of  $2.5 \times 10^{-18}$  cm<sup>2</sup>.

A preliminary photoionization experiment employing the same instrumentation demonstrated the appearance of the ionization current at 1345 Å or 9.20 eV. From previous experiments on light intensity measurements from thermocouple data photoionization was found to account for about fifty percent of the total absorption at Lyman-alpha. The ionization cross section for NO as determined by the authors of the present paper is about twenty-five times larger than the theoretical value by Bates and Seaton (1950).

The width and the transparency of the oxygen windows in the spectral region 1100–1300 Å appear to



indicate that photons of required energy, particularly Lyman-alpha, can penetrate deep into the D-layer. This work appears to lend support to the following mechanism for the formation of the D layer.



WATANABE, K., MARMO, F., AND INN, EDWARD C. Y., "Photoionization of Nitric Oxide," *Phys. Rev.* **91**, 436 (1953).

In a paper read before the Spring Meeting of the American Physical Society held at Washington, D. C. 30 April, 1 and 2 May 1953 the authors reported the results of their measurements of the ionization cross section of nitric oxide in the spectral region 1070-1345 Å. During the scanning of the spectrum photoionization occurred abruptly at  $\lambda$  1345 Å or  $9.20 \pm 0.02$  eV which was considered to be the first ionization potential of NO.

The ionization cross section was found to represent a rather high fraction of the total absorption cross section over most of the spectral region studied. At Lyman-alpha the ionization cross section had a value of about  $1.5 \times 10^{-18} \text{ cm}^2$  while the total absorption cross section was about  $2.5 \times 10^{-18} \text{ cm}^2$ . These data and the absorption cross section of oxygen were considered applicable to the formation of the D layer.

WATANABE, K., MARMO, F. F., AND INN, EDWARD C. Y., "Photoionization Cross Sections of Nitric Oxide," *Phys. Rev.* **91**, 1155 (1953).

The measurement of the photoionization cross section of nitric oxide in the spectral region  $\lambda\lambda$  1070-1343 Å is described. The purpose of the determination of the photoionization cross section of nitric oxide was to find out if the formation of the D layer of the atmosphere might be caused by the ionization of the nitric oxide molecule by solar radiation within this spectral range.

The results are shown in Table I in the paper for pressures 0.49 to 10.5 mm Hg. The values obtained are apparently independent of pressure and nearly constant with respect to wavelength in the spectral region studied. The total absorption cross section of nitric oxide was found to be about fifty times higher than the theoretical value calculated by Bates and Seaton (*Proc. Phys. Soc. (London)* **63B**, 129 (1950)). The photoionization cross section at Lyman-alpha was  $1.24 \times 10^{-18} \text{ cm}^2$  which is about one-half the total absorption cross section. The total cross section is given by the following equation.

$$I = I_0 \exp(-\sigma n_0 x)$$

Where  $I_0$  and  $I$  are the incident and transmitted light intensities,  $\sigma$  is the total absorption cross section in  $\text{cm}^2$ ,  $n_0$  is the number of molecules per  $\text{cm}^3$  at N. T. P., and  $x$  is the thickness in cm of the layer of absorbing gas at N. T. P.

Since it cannot be assumed that all of the absorbed photons will produce photoionization, the total absorption cross section,  $\sigma$ , is set equal to the following expression

$$\sigma = \sigma_1 + \sigma_2$$

where  $\sigma_1$  represents the photoionization cross section, and  $\sigma_2$  the cross section for other purposes. To determine the value of (photoionization cross section) the authors give the equation

$$\sigma_1 = N_1 \sigma / N$$

in which  $\sigma$  is the total absorption cross section previously determined by the authors,  $N$  is the number of photons absorbed per second in the length corresponding to the length of the collecting electrode ( $N$  being

found from previously determined  $\sigma$  values); and  $N_1$  is the number of ions formed per second in the same path length being obtained from the ion current.

The present paper also gives a new method for the determination of ionization potentials of molecules in the vacuum ultraviolet for nitric oxide and other molecules. The first ionization potential for nitric oxide (NO) was found to be  $9.23 \pm 0.02$  ev. Reference is made to the authors' previous paper (*Phys. Rev.* 90, 155 (1953)) in regard to the application of the method to the formation of the D layer.

WEBER, D., AND PENNER, S. S., "Rotational Line-Width Measurements on NO, HCL and HBr," *J. Chem. Phys.* 21, 1503 (1953).

In this paper apparent line-widths measurements on diatomic gases of interest in connection with attempts to calculate emissivities from spectroscopic data were made. Rotation half-widths were calculated from the experimental data assuming that the rotational lines are described by the Lorentz collision formula and that they were uniform half-width for a given vibration-rotation band.

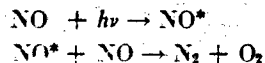
The term rotation half-width is used to denote one-half of the wave-number range for which the spectral absorption coefficient exceeds one-half of the maximum value for a given rotational transition. The value of the apparent half-width of the fundamental for NO is given as  $0.043 \text{ cm}^{-1} \text{ atmos}^{-1}$ , and  $0.031 \text{ cm}^{-1} \text{ atmos}^{-1}$  with helium added. The quantitative measurements are described.

#### 1954

GAYDON, A. G., AND FAIRBAIRN, A. R., "Pressure Broadening in the Spectrum of NO and Its Photodissociation," *Proc. Phys. Soc. (London)* 67 A, 474 (1954).

The authors have made an examination of the absorption spectrum of nitric oxide (NO). The study is of importance because of its application to the dissociation energies of NO and  $N_2$ . Gaydon (1953) favors the high value of 9.76 ev for  $D(N_2)$ . If proved, induced predissociation would require the low value of 7.38 ev for  $D(N_2)$ . A brief description is given of the instrumentation and experimental procedure. The authors have re-examined the interpretation of the photodissociation of NO. Reference is made to the work of Flory and Johnston (1935) who found that the active region was probably located in a band of the system at 1830 Å. In an experiment in which nitric oxide was exposed through quartz to an iron arc at a distance of about two inches for two days Gaydon (1953) did not detect any  $NO_2$  formation.

The authors conclude that the action in the spectral range employed must be very slight and have a low quantum efficiency. The following mechanism is included to explain the small amount of dissociation by the secondary reaction



This mechanism is similar to Gaydon's (1953) explanation for the dissociation of carbon monoxide. It is concluded that there is no abnormal pressure broadening and hence no induced predissociation in nitric oxide. Consequently this weak dissociation is not of importance in the dissociation energies of NO and  $N_2$ .

MITRA, A. P., "A Tentative Model of the Equilibrium Height Distribution of Nitric Oxide in the High Atmosphere and the Resulting D-Layer," *J. Atm. Terrest. Phys.* 5, 28 (1954).

Reference is made to the spectrum of the sun which was taken during a rocket flight. Durand (1949)

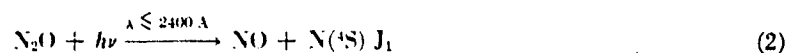
interpreted the broad band lying between  $\lambda$  2200-2300 Å to be due to nitric oxide (NO). Later Tousey indicated that the band may have been caused by NO existing in the atmosphere of the sun.

The author in the present paper has attempted to derive a tentative model for the equilibrium distribution of nitric oxide (NO) in the height range 50-100 km of the atmosphere. Mitra arrives at his conclusion by considering possible photochemical reactions involving ozone, both atomic and molecular nitrogen and oxygen, and nitrous oxide. Two possible processes for the production of NO in the upper atmosphere are given.

First a three-body recombination between atomic oxygen and nitrogen and a third body.



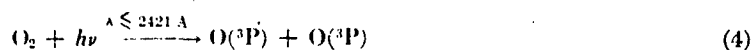
The second mechanism suggested by Bamford (1943), Gaydon (1947), and Nicolet (1952) is the photodissociation of  $\text{N}_2\text{O}$  into N and NO.



The presence of atomic oxygen in the lower atmosphere is due to the photodissociation of  $\text{O}_2$  in the Schumann-Runge absorption continuum beginning at  $\lambda$  1759 Å.



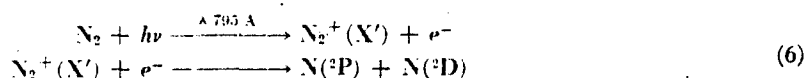
and also in the weak Herzberg continuum.



Two processes are also given for the presence of atomic nitrogen in the upper atmosphere. The Herzberg-Herzberg (1943) process regards molecular nitrogen to be predissociated by absorption in the Lyman-Birge-Hopfield band  $\lambda\lambda$  1150-1250 Å.



The second process, known as the dissociation recombination mechanism, has been discussed both by Bates (1950), and by S. K. Mitra (1951).



The latter process was considered by Deb (1952) to be important only above about 170 km, while the former process is effective in the lower ionospheric regions.

The two reactions considered favorable for the production of  $\text{N}_2\text{O}$  by homogeneous gas reactions are those in which (a) atomic oxygen (O), and (b) ozone ( $\text{O}_3$ ) are the parent particles.



Thus two different height distributions are computed for  $\text{N}_2\text{O}$  corresponding to reaction (8) in which the concentration of  $\text{N}_2\text{O}$  decreased rapidly with height, and reaction (7) where the decrease is slower.

The distribution of nitric oxide (NO) will depend, of course, on the types of atomic oxygen and  $\text{NO}_2$  distributions assumed. The author concludes that in general, under conditions of photochemical equilibrium, the maximum concentration of NO occurs at an altitude of about 85-95 km, and that the maximum

concentration does not exceed a value of about  $2 \times 10^{12} \text{ cm}^{-3}$ . The role of photoionization of NO by Lyman-alpha radiation in the formation of the D-layer is also briefly discussed.

MITRA, A. P., AND JONES, R. E., "The Enhancement of Ionospheric Ionization during Solar Flares," *J. Atm. Terrest. Phys.* 5, 104 (1954).

Brief reference is made to the enhancement of Lyman-alpha ( $L_\alpha$ ) radiation. It is suggested that an increase or generation of ionization through direct photoionization is a reasonable assumption for the occurrence of fadeout enhancement of ionization. The relevant process is the ionization of NO by enhanced  $L_\alpha$  radiation. There appears to be evidence that such enhancement occurs.

MIZUSHIMA, MASATAKA, "Theory of the Hyperfine Structure of NO Molecule," *Phys. Rev.* 94, 569 (1954).

This paper by Mizushima from the Department of Physics, Duke University, Durham, North Carolina is a report on research supported by the U. S. Air Force under a contract monitored by the Office of Scientific Research, Air Research and Development Command. The paper gives the theory of the hyperfine structure of the NO molecule due to the magnetic moment of the N nucleus. The electronic ground state of the NO molecule is  $\Pi_{1/2}$ .

The topics discussed are:

- (1) Hamiltonian and Wave Function.
- (2) Magnetic Hyperfine Structure.
- (3) Electric Hyperfine Structure.
- (4) Effect of  $\Pi_{3/2}$  State.
- (5) Comparison with Experimental Results.
- (6) Prediction of the HFS of the NO Molecule in the  $\Pi_{3/2}$  State.
- (7) Electric HFS Formula for General Coupling Case.

NIGHTINGALE, R. E., DOWNIE, A. R., ROTENBERG, D. L., CRAWFORD, BRYCE, JR., AND OGG, R. A., JR., "The Preparation and Infrared Spectra of the Oxides of Nitrogen," *J. Phys. Chem.* 58, 1047 (1954).

This paper gives improved laboratory preparations of several oxides of nitrogen. The purpose was to provide pure nitrogen oxides suitable for investigation of the kinetics of reactions of the oxides of nitrogen, and to use the infrared spectra of these molecules for identification, or analysis.

Nitric oxide (NO) was used as the basic starting material for the preparation of all of the oxides whose preparations are discussed. Methods for the preparation of nitric oxide, nitrogen dioxide-dinitrogen tetroxide ( $\text{NO}_2$  in equilibrium with  $\text{N}_2\text{O}_4$ ), ozone, nitrogen pentoxide, and anhydrous nitric acid are described.

The infrared spectra of the nitrogen oxides were examined in the rock-salt region ( $650\text{--}2500 \text{ cm}^{-1}$ ) to find the absorption bands suitable for analytical purposes. The more intense infrared bands of the oxides of nitrogen are shown in Figure 3 of the paper. Particular emphasis is given to obtaining the spectrum of nitrogen pentoxide ( $\text{N}_2\text{O}_5$ ) free from water.

OPFELL, J. B., SCHLINGER, W. G., AND SAGE, B. H., "Some Thermodynamic Properties of Nitric Oxide," *Ind. Eng. Chem.* 46, 189 (1954).

A brief review of the thermodynamic properties of nitric oxide investigated by previous workers is given. The expressions for enthalpy, entropy, and fugacity are combined with the relationships for pressure

and isochoric pressure-temperature derivative. These are shown in Table II in the paper. The expressions in Table II were used to obtain the desired expressions for these thermodynamic properties. The properties listed in Table III which is extensive are values of pressure, volume, enthalpy, entropy, and fugacity. The data were based on a reference state of zero for the enthalpy and entropy at a temperature of absolute zero and a pressure of 1 atmosphere for the ideal gas state. This corresponds to the convention adopted by Rossini (1950).

TANAKA, YOSHIO, "Emission Bands of NO in the Vacuum Ultraviolet Region Excited in the NO Afterglow," *J. Chem. Phys.* 22, 2045 (1954).

Briefly this is an investigation of the emission bands of the NO molecule excited in an afterglow in the vacuum ultraviolet region. The author reports that there is an abrupt cutoff at a certain value of  $\nu'$ . This was observed in the  $\beta$ ,  $\gamma$  and  $\delta$  bands.

WATANABE, K., "Photoionization and Total Absorption Cross Sections of Gases. I. Ionization Potentials of Several Molecules. Cross Sections of  $\text{NH}_3$  and NO," *J. Chem. Phys.* 22, 1564 (1954).

In the present paper Watanabe reports the determination of ionization potentials of several molecules. The ionization potential for NO is included and was determined to be 9.25 electron volts. The paper also describes improved energy measurements of the photoionization cross sections of NO in the spectral region  $\lambda\lambda$  1070-1340 Å. The results obtained earlier by the author (*Phys. Rev.* 91, 1155 (1953)) were found in the present study to be about 40 percent too low. The photoionization and the total cross section of NO at Lyman-alpha (1215.6 Å) were  $2.0 \times 10^{-18}$  and  $2.4 \times 10^{-18}$  cm<sup>2</sup>, respectively. An absorption was suggested to explain this difference.

#### 1955

KAUFMAN, FREDERICK, AND JOHN R. KELSO, "Thermal Decomposition of Nitric Oxide," *J. Chem. Phys.* 23, 1702 (1955).

The thermal decomposition of pure NO was studied and found to be second order in NO throughout the course of decomposition. The second-order rate constants defined by

$$-d(\text{NO})/dt = k(\text{NO})^2$$

represent the data quite well.

The relative importance of homogeneous surface effects were studied. The effects of added nitrogen, helium, and oxygen were investigated. Experimental details of the instrumentation, the preparation and analyses of the reactant gases, and products are fully described. An interpretation is given and a mechanism is discussed on the oxygen effect.

NICHOLS, NATHAN L., HAUSE, C. D., AND NOBLE, R. H., "Near Infrared Spectrum of Nitric Oxide," *J. Chem. Phys.* 23, 57 (1955).

Nitric oxide is the only stable diatomic molecule to exhibit a Q branch in the infrared, since it is the only stable diatomic molecule to have an odd number of electrons. A brief discussion is given of the first observance of the infrared spectrum of NO by Warburg and Leithauser (*Ber. deut. chem. Ges.* 1, 145 (1908)).

Experimental details of the present paper are included. The molecular rotational constants for the ground state both for values obtained by the authors and the vibrational constants obtained by Gillette and Eyster (*Phys. Rev.* 60, 113 (1939)) are given in the following table.

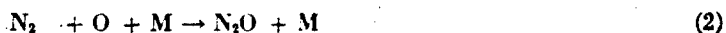
$\omega_{e1} = 1904.03 \text{ cm}^{-1}$	$B_e = 1.7060 \text{ cm}^{-1}$
$\omega_{e2} = 1903.68 \text{ cm}^{-1}$	$\alpha_e = 0.0180 \text{ cm}^{-1}$
$\omega_e X_e = 13.97 \text{ cm}^{-1}$	$I_e = 16.404 \times 10^{-40} \text{ g cm}^2$
$\omega_e Y_e = 0.00120 \text{ cm}^{-1}$	$r_e = 1.1503 \times 10^{-8} \text{ cm}$
$D_e = 6.8 \times 10^{-8} \text{ cm}^{-1}$	

NICOLET, MARCEL, "The Aeronomic Problem of Nitrogen Oxides," *J. Atm. Terrest. Phys.* 7, 152 (1955).

A brief summary is given of Nicolet's previous announcement (*Inst. Roy. Meteorol. Belgium Memoirs* 19, 124 (1945)) that nitric oxide is an important constituent of the high atmosphere. In this earlier paper it was considered that nitric oxide could be quite abundant below the transition in which atomic oxygen is formed from the dissociation of molecular oxygen. It was thought that the nitric oxide molecule could explain the ionization below 100 km. Since the ionization potential is about 9.5 eV Nicolet pointed out that this molecule could absorb the Lyman  $-\alpha$  solar radiation at  $\lambda$  1215.7 Å.

Reference is made to Bates and Seaton (1950) who gave reasons for the difficulty in considering any other mechanism for example the photoionization of  $O_2$  or Na. Reference is also made to the measurement of absorption coefficients of NO,  $O_2$  and other molecules by Watanabe, Marmo and Inn (1953) who concluded that the formation of the D region was due to the absorption of Lyman  $-\alpha$  radiation which lies in an atmospheric window.

Two mechanisms are given for the formation of nitric oxide in the mesosphere.



Reaction (1) is considered the primary process of NO formation. In a region in which atomic oxygen concentration is maximum, process (2) should yield NO. Reference is made to the study of absorption coefficients of nitrous oxide ( $N_2O$ ) by Zelikoff, Watanabe and Inn (1953), and by Zelikoff and Aschenbrand (1954) who interpreted absorption continua in terms of other possible dissociation processes. According to their conclusions process (2) is not considered a fundamental mechanism for the production of nitric oxide and atomic nitrogen.

SUN, H., AND G. L. WEISSLER, "Absorption Coefficients of Nitric Oxide in the Vacuum Ultraviolet," *J. Chem. Phys.* 23, 1372 (1955).

In this letter to the editor the authors report their preliminary results of the absolute absorption of light in NO in the region from 374 Å to 1300 Å. Photometric measurements of 60 light source emission lines were obtained. The coefficients  $\mu$ , in units of  $\text{cm}^{-1}$  at NTP, are defined by the relation

$$I = I_0 \exp(-\mu x).$$

The authors state that previous NO results between 1100 Å and 2300 Å obtained by Marmo (1953) and Watanabe (1954) were in reasonable agreement with those in the present report in the spectral region where overlapping occurred. A table of absorption coefficients of NO in the region studied is included.

2.3 NITROGEN DIOXIDE (NO<sub>2</sub>) AND OTHER OXIDES OF NITROGEN

1910

HAYHURST, WALTER, AND PRING, JOHN NORMAN, "The Examination of the Atmosphere at Various Altitudes for Oxides of Nitrogen and Ozone," *J. Chem. Soc.* 97, 868 (1910).

The authors emphasize that the results of their experiments are to be considered of a purely qualitative nature. The amount of ozone was too small to be detected at ground level and at intermediate altitudes up to 8500 feet.

Attempts were made to determine and compare the amount of the oxides of nitrogen at different altitudes. Some 15 experiments were conducted at ground level (1100 feet above sea level), and 30 experiments were at intermediate heights up to 8500 feet. For these measurements a kite was used to carry an absorbing vessel containing a solution of potassium iodide, and exposed at known altitudes. The altitude of the kite and wind velocities were obtained by means of the Dines recording meteorograph (*Nature* 83, 220 (1910)). The data from the six most successful experiments are tabulated.

Maximum Height in Ft.	Ratio Oxides of Nitrogen in Upper to that in Lower Atmosphere
8500	2.23 : 1
3200	1.74 : 1
2600	1.76 : 1
4200	1.20 : 1
4500	0.93 : 1
4500	0.90 : 1

Note: These experiments were on different dates.

It was concluded that a rather greater amount of oxides of nitrogen occurred at higher altitudes than at ground level for equal volumes of air, and that the total amount of the oxides appeared to vary from day to day, and much less present after rain. With the aid of free balloons an examination of the atmosphere at high altitudes up to a height of about 12 miles was made. In general the same method was employed for the determination of the oxides of nitrogen and of ozone as in the experiments at intermediate heights with a kite. The amount of ozone averaged 0.04 milligram in 0.1 to 0.3 cubic meters of air, while the amount of oxides of nitrogen was shown to be less than this quantity.

1923

REYNOLDS, WILLIAM C., "Thunderstorms and Ozone," *Nature* 112, 396 (1923).

In an attempt to answer the question as to what chemical changes, if any, are associated with atmospheric electrical discharges, the author has studied the formation of nitrogen dioxide and ozone during a severe thunderstorm over London 10 July 1923. The following results were obtained for the analysis of NO<sub>2</sub> in terms of one volume of NO<sub>2</sub> in million volumes of air.

Nitrogen Dioxide Before, During and After the Thunderstorm			
	Before	During	After
London air	1 in 120	1 in 114	1 in 134
Upminster air (country)	1 in 350	1 in 440	1 in 400

It was concluded that there was no appreciable increase in nitrogen dioxide in the air during the storm.

Ozone Concentration Before and After Thunderstorms in England

	A Few Days Before	After	A Fortnight After
London air	1 in 23	1 in 3.2	1 in 18.5
Upminster	1 in 22	1 in 14.8	1 in 18.5
Storm No. 2			
London	1 in 22.7	1 in 9.71	
Upminster	1 in 18.8	1 in 7.8	

During the first thunderstorm 7 times more ozone were found after the storm than before in the air above London. A fortnight afterwards one part in 18.5 millions were found in both places. For storm No. 2 more than double in each case was found before than after the thunderstorm.

### 1925

FRANCIS, A. G., AND PARSONS, A. T., "The Determination of Oxides of Nitrogen (except Nitrous Oxide) in Small Concentrations in the Products of Combustion of Coal Gas and in Air," *Analyst* 50, 262 (1925).

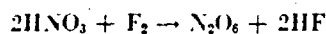
This is an extensive and thorough study on the determination of small concentrations of the oxides of nitrogen in coal gas and in air. The method of Allison, Parker and Jones reported in Technical Paper 249, Bureau of Mines, Washington, D. C. which consisted in absorbing the oxides in an alkaline solution of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) was found to give incomplete oxidation. The authors report a modification of the alkaline- $\text{H}_2\text{O}_2$  method. Their procedure was to aspirate the gas sample through a bottle of known capacity, adding  $\text{H}_2\text{O}_2$  acidified with sulfuric acid ( $\text{H}_2\text{SO}_4$ ), and allowing the sample bottle to stand with frequent shaking for 3 hours. The solution was rinsed into an evaporating dish, neutralized with KOH solution, and evaporated to dryness.

The residue was determined colorimetrically with phenoldisulfonic acid reagent, making alkaline with  $\text{NH}_4\text{OH}$  and comparing with color standards. The method was sensitive to over 1 part per million of NO present in air. The method is capable of increased sensitivity to a few parts of NO in one hundred million by condensing the dried air sample with liquid air, the  $\text{CO}_2$  and NO in the air condenses and the latter was analyzed by the above procedure of the condensate. A correlation of the amount of oxides of nitrogen present with motors about, during foggy weather, after heavy rains, and during clear weather is shown with a brief discussion of the data obtained.

### 1929

FICHTER, FR., AND BRUNNER, ERNST, "Oxidation with Fluorine. III. Action of Fluorine on Nitric Acid, Perchloric Acid and Their Compounds," *Helv. Chim. Acta* 12, 305 (1929).

When an aqueous solution of  $\text{HNO}_3$  was treated with gaseous fluorine the following reaction was observed to occur:



NOTES. RONALD G. W., "Photochemical Equilibrium in Nitrogen Peroxide. Part IV. The Relation between Fluorescence and Photochemical Action," *J. Chem. Soc.* (1929), pp. 1611-1620.

The fluorescence of nitrogen dioxide was detected and photographed. Blue light of wavelength 4360 Å produced an orange luminescence, and violet light  $\lambda$  4050 Å a greenish-yellow luminescence. From the



observations it was concluded that in the pure gas the  $\text{NO}_2$  molecule, excited by the absorption of blue or violet light, may suffer many molecular collisions before it re-emits its energy. This would explain the rather wide diffuse emission bands.

## 1930

BAXTER, WARREN P., "Quenching of the Fluorescence of Nitrogen Dioxide," *J. Am. Chem. Soc.* 52, 3920-3927 (1930).

The author refers to the several investigations of the photochemical decomposition of nitrogen dioxide, particularly to the work of Norrish (1927 and 1929). In the present paper nitrogen dioxide was irradiated with  $\lambda$  4358 and 4047 Å lines of a mercury arc and a pressure range 0.001 to 18 mm Hg. The purpose of the study was to investigate the intensity of the fluorescence of  $\text{NO}_2$  itself and of added foreign gases.

Nitrogen dioxide was found to be a very efficient quenching agent, the fluorescence was half damped at a pressure of 0.02 mm. The relative deactivational efficiencies of the foreign gas  $\text{CO}_2$ ,  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{H}_2$  referred to  $\text{NO}_2$  as unity are, respectively, 0.87, 0.29, 0.24, and 0.15.

REYNOLDS, WILLIAM C., "Notes on London and Suburban Air," *J. Soc. Chem. Ind. (Trans.)* 49, 168-172 (1930).

The author made continuous measurements of chlorides, ammonia, nitrogen dioxide, sulfur dioxide, and ozone on London and suburban air from 1923 to 1927.

With reference to nitrogen dioxide the author states that it is essentially a constituent of town air. No evidence was obtained that it is formed by the action of lightning, since at no time did the proportion of nitrogen dioxide in the atmosphere increase during thundery weather. The amount of  $\text{NO}_2$  measured at Upminster (suburban) was generally about one sixth of that found at Plaistow (about 5 miles from London Bridge). In the latter place it rose to as much as 30 volumes per 1000 million in foggy weather. The existence of ozone at sea level has been attributed to nitrogen dioxide.

A detailed description of the analytical methods and sampling are included.

## 1931

SPRENGER, GERHARD, "Spectrographic Identification of the Intermediate Nitrogen Oxide in the Reaction between Nitrogen Pentoxide and Ozone," *Z. Electrochem.* 37, 674-678 (1931).

In this report Sprenger discusses the spectrographic evidence for the evidence of and formation of nitrogen trioxide,  $\text{NO}_3$ , in the reaction of nitrogen pentoxide with ozone.

## 1934

HOLMES, HARRISON H., AND DANIELS, FARRINGTON, "The Photolysis of Nitrogen Oxides:  $\text{N}_2\text{O}_5$ ,  $\text{N}_2\text{O}_4$ , and  $\text{NO}_2$ ," *J. Am. Chem. Soc.* 56, 630-637 (1934).

Reference is made to the careful work of Baxter and Dickinson (1929) on the photolysis of nitrogen pentoxide; and to Norrish (1929), and Dickinson and Baxter (1928) on nitrogen dioxide. These workers established the general nature of the reaction. In the present study Holmes and Daniels have extended this work to a wider range of observation, particularly at short wavelengths (436  $\mu$  to 265  $\mu$ ).

The absorption coefficients at wavelengths from 436 to 265  $m\mu$  were determined for  $N_2O_3$ ,  $N_2O_4$  and  $NO_2$ . It was found that  $N_2O_3$  was decomposed by the light absorbed at 280 and 265  $m\mu$  with a quantum efficiency of 0.6. Nitrogen tetroxide was observed to decompose at 265  $m\mu$  with a quantum efficiency of 0.4, while light at wavelengths 366  $m\mu$  and 313  $m\mu$  was absorbed with no measurable decomposition of  $N_2O_4$ . The following wavelengths decomposed  $NO_2$  with the accompanying quantum efficiencies: 313  $m\mu$ , 1.93; 366  $m\mu$  1.83; 402 (at 0°C), 0.50; and 436  $m\mu$ , 0.0 (after allowance for the screening effect of  $N_2O_4$ ).

The effect of He, A,  $N_2$ ,  $O_2$ ,  $H_2$ ,  $CO_2$  and  $N_2O$  in decreasing the photodecomposition of  $NO_2$  was determined.

Wavelength $m\mu$	Absorption Coefficients		
	$k$	$1/p \ln I_0/I$	
	$k_{NO_2}$	$k_{N_2O_4}$	$k_{N_2O_3}$
436	0.0192	0	0
405	0.0216	0	0
366	0.0187	0.00824	0
334	0.013	0.015	0
313	0.00773	0.0119	0
302	0.0055	0.0085	0
280	0.00263	0.0174	0.0029
265	0.00136	0.0243	0.0063

STODDART, ERIC M., "The Oxygen Afterglow," *Proc. Roy. Soc. (London) A* 147, 454 (1934).

A description of the electrodeless discharge apparatus is given. With reference to the role of nitric oxide it is stated that the afterglow is restored by the addition of nitrogen to glowless oxygen in electrode discharge tubes. This phenomenon is not observed when electrodeless tubes are used.

The following conclusions were noted as a result of the experiments described in the paper. (a) Ordinary electrode discharges through oxygen-nitrogen mixtures readily synthesized nitric oxide, whereas the formation of NO did not occur if electrodeless discharges were employed. (b) The addition of nitric oxide to an electrodeless discharge through pure oxygen produced an afterglow. (c) The afterglow spectrum  $\lambda$  4200 A to 6700 A consisted of weak diffuse bands.

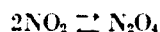
1935

MELVIN, EUGENE H., AND WULF, OLIVER R., "Ultraviolet Absorption of Mixtures of NO,  $NO_2$ , and  $H_2O$ ," *J. Chem. Phys.* 3, 755 (1935).

The authors state that in considerable amounts of NO containing small amounts of  $NO_2$  a continuous absorption occurs in the ultraviolet which obscures both the absorption of NO and that portion of the absorption which lies below 2500 A. This is considered to be due to the molecule  $N_2O_3$ .

In Figure 1 in the paper the absorption bands occurring in mixtures of NO,  $NO_2$ , and  $H_2O$  (probably due to  $HNO_2$ ), together with a comparison spectrum of  $NO_2$ , are shown. Figure 2 in the paper shows the effect of increasing nitrogen dioxide ( $NO_2$ ) to a constant pressure mixture of NO and  $H_2O$ , and similarly the effect of increasing nitric oxide to a constant pressure of  $NO_2$  and  $H_2O$ . In Figure 3 in the paper the influence of  $H_2O$  upon a mixture of NO and  $NO_2$ , and the temperature effect are shown.

The question is raised as to the  $N_2O_3$  content of "pure  $NO_2$ ," since in a mixture of as pure



as one can prepare there exists the equilibrium



NEWMAN, F. H., "Air Afterglows," *Phil. Mag.* 20, 777 (1935).

This is a study of the spectra of air and oxygen afterglows. It was found that with air the afterglow was at first very faint at all pressures, but after the discharge had been passed for some time the intensity increased. The results obtained in this investigation lead to the conclusion that both oxygen and air afterglows arise from the oxidation of nitric oxide by ozone, both nitric oxide and ozone being formed in the discharge tube. The product thus formed (a higher oxide of nitrogen) gave rise to the faint diffuse bands between  $\lambda$  4200 Å and  $\lambda$  6700 Å.

SPEALMAN, M. L., AND RODEBUSH, W. H., "The Reactions of Some Oxides of Nitrogen with Atomic Oxygen and Nitrogen," *J. Am. Chem. Soc.* 57, 1474-1476 (1935).

Reference is made to the role played by the oxides of nitrogen in the nitrogen and oxygen afterglows. The following reactions were studied. (a) The reaction between nitrogen dioxide and oxygen atoms produces a characteristic oxygen afterglow according to the reaction,



(b) The reaction between nitric oxide and oxygen atoms is the reverse of the photochemical decomposition of nitrogen dioxide.



Reference is made to Norrish (1929), Dickinson and Baxter (1928), and Mecke (1930) who studied this reaction. Mecke had concluded that light of  $\lambda$  3700 Å decomposed  $NO_2$  according to reaction (2). When nitric oxide was introduced into pure oxygen gas which is partially dissociated into atomic oxygen, the oxygen afterglow was obtained. It is concluded that the reaction,



which presumably takes place by triple collision causes the oxygen afterglow.

### 1937

JONES, ERNEST J., AND WULF, OLIVER R., "The Absorption Coefficient of Nitrogen Pentoxide in the Ultra-violet and Visible Absorption Spectrum of  $NO_3$ ," *J. Chem. Phys.* 5, 873-877 (1937).

The authors obtained spectrograms of the gaseous system  $N_2O_5-O_3$  during the decomposition of the ozone and the subsequent decomposition of  $N_2O_5$ . By a suitable arrangement in experimental details it was possible to obtain spectrograms when the absorption was chiefly that of  $NO_3$  (nitrogen trioxide).

In course of time the  $NO_3$  and  $O_3$  steadily decreased, the contents of the absorption tube passing from that of visually blue through a colorless stage which was followed by the appearance of brown fumes of  $NO_2$ . At this point of absence of both ozone and nitrogen dioxide a spectrophotometric determination of the intensity of  $N_2O_5$  in the ultraviolet was made. The absorption coefficients,  $\alpha_{10}$ , of  $N_2O_5$  was measured over the wavelength region 3800-2850 Å. The value obtained at 3800 Å was 0.002, and steadily increased to approximately 0.52 at 2850 Å.

At the time when the absorption tube was visually blue when the absorption was due chiefly to  $\text{NO}_3$ , satisfactory spectrograms were obtained for  $\text{NO}_3$ . The experimental details are described in full, as well as the results and subsequent discussion. The  $\text{NO}_3$  is an "odd" molecule, containing an odd number of electrons, which may account for its intense blue color.

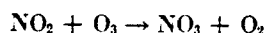
KLEMENC, ALFONS, AND NEUMANN, WALTER, "Investigation of the Formation of a Higher Oxide of Nitrogen ( $\text{NO}_3$ ) in the Action of a Glow Discharge of Gaseous Systems of  $\text{NO}_2$ - $\text{O}_2$ ," *Z. anorg. allgem. Chem.* **232**, 216 (1937).

The authors have investigated the possibility of the formation of a higher oxide of nitrogen such as ( $\text{NO}_3$ ) by passing a glow discharge through  $\text{NO}_2$ - $\text{O}_2$  mixtures. They report that no such compound as  $\text{NO}_3$  was obtained. The nitrogen dioxide was about 95 percent decomposed in the discharge and excess oxygen had no effect upon the reaction.

The authors state that nitrogen trioxide ( $\text{NO}_3$ ) can only be obtained by vaporization of a gas mixture of nitrogen dioxide and ozone.

SCHUMACHER, H. J., "Nitrogen trioxide ( $\text{NO}_3$ )," *Z. anorg. allgem. Chem.* **233**, 47 (1937).

This is a report on the formation of nitrogen trioxide ( $\text{NO}_3$ ) by the reaction of nitrogen dioxide with ozone.



This reaction is followed by the reaction of the  $\text{NO}_3$  produced with additional  $\text{NO}_2$ .



Under a given set of conditions a definite concentration of  $\text{NO}_3$  can be obtained since the  $\text{N}_2\text{O}_5$  liberates a definite amount of  $\text{NO}_2$  which may react with  $\text{O}_3$ .

#### 1938

ADEL, ARTHUR, AND LAMPLAND, C. O., "The Discovery of a New Constituent in the Earth's Upper Atmosphere, Nitrogen Pentoxide," *Bull. Am. Meteorol. Soc.* **19**, 33 (1938).

This is an abstract of a paper given at the joint session with Section D (Astronomy) at the Indianapolis Meeting 27-29 December 1937 of the American Meteorological Society. Adel and Lampland reported at the Meeting their discovery of the presence of nitrogen pentoxide as a new constituent in the high atmosphere. The location in the atmosphere of the new constituent is probably coincident with the ozone layer (10 to 25 miles above sea level).

The discovery was made spectroscopically by observations in the far infrared region of the spectrum. A humid atmosphere obscures the infrared spectrum of the new constituent. The dry air above the Lowell Observatory (Arizona) was essential. It was suggested that the new constituent is the photochemical resultant of atmospheric nitrogen, oxygen, and ozone.

#### 1939

ELKINS, HERVEY B., "Toxic Fumes — In Massachusetts Industries," *Industrial Med.* **8**, 426 (1939).

This is a report by Hervey B. Elkins, Chemist, Massachusetts Division of Occupational Hygiene, Boston. The author states that most occupational diseases fall roughly into one of three groups:

- (1) Dust diseases.
- (2) Occupational dermatoses.
- (3) Poisoning by toxic fumes and gases.

In order to obtain data on as many toxic fumes as possible the author prepared a table of existing threshold, or maximum allowable concentrations of solvents and gases known to be toxic. This list was sent to some 19 American and 8 foreign authorities. The suggestions and criticisms of the replies from this questionnaire were tabulated and considered in detail by the Massachusetts Dust and Fume Code Committee. From a careful study of this evidence and additional literature research the maximum allowable concentrations (threshold) for some 40 substances were proposed.

This is probably the most complete and thorough compilation of maximum allowable concentrations for industrial gases and fumes prepared up until 1939. A few of the toxic gases are listed in the table below from which  $\text{NO}_2$  may be compared with some of the better known toxic gases.

Gases	Threshold Concentration ppm
Nitrogen dioxide	10
Hydrogen sulfide	20
Hydrogen cyanide	20
Ozone	1
Chlorine	1
Carbon monoxide	100
Ammonia	100
Sulfur dioxide	10

## 1941

BARBIER, D., CHALONGE, D., AND MASRIERA, M., "The Afterglow Accompanying the Thermal Decomposition of Ozone," *Compt. rend.* 212, 984-986 (1941).

These investigators observed that above  $150^\circ\text{C}$  the decomposition of ozone is accompanied by radiation of light which increased with rising temperature. Ozone from air or nitrogen containing some oxygen produced a strong afterglow. If the ozone was prepared from pure oxygen containing only traces of nitrogen the afterglow was weak. The spectrum is continuous and extends from  $\lambda$  3850 Å to  $\lambda$  6500 Å. The diffuse bands are due to nitrogen dioxide.

EDGAR, J. L., AND PANETH, F. A., "The Separation of Ozone from Other Gases," *J. Chem. Soc.* (1941), pp. 511-519.

The method described by Edgar and Paneth in the present paper is based on the condensation of ozone on the surface of specially prepared silica gel, and its separation from other gases by fractional distillation. Ozone in any degree of dilution when passed over silica gel cooled in liquid oxygen can be frozen out quantitatively, and recovered without decomposition by subsequently raising the temperature of the silica gel.

The separation of ozone from nitrogen dioxide in atmospheric air is described. The boiling point of nitrogen dioxide is about  $22^\circ\text{C}$ , making it possible to keep  $\text{NO}_2$  in the condensed state on the surface of the silica gel while distilling off the ozone (boiling point  $-112.3^\circ\text{C}$ ). It was found that when both gases ( $\text{O}_3$  and  $\text{NO}_2$ ) were first condensed on silica gel in a trap in liquid oxygen, the temperature afterwards raised to  $-120^\circ\text{C}$  while a current of oxygen gas was passed over the gel, the ozone was obtained quantitatively and no traces of nitrogen dioxide could be detected in the effluent gas.

EDGAR, J. L., AND PANETH, F. A., "The Determination of Ozone and Nitrogen Dioxide in the Atmosphere," *J. Chem. Soc.* (1941), pp. 519-527.

The method described by the authors in the preceding paper (*J. Chem. Soc.* (1941), 511-519) demonstrated that  $\text{NO}_2$  and  $\text{O}_3$  could be sharply separated by adsorption on silica gel and subsequent distillation in a current of oxygen at a temperature not exceeding  $-120^\circ\text{C}$ . The nitrogen dioxide remains absorbed.

The analytical determination of the  $\text{NO}_2$  was accomplished by attaching the cooled trap to an evacuated vessel of about 3-liter capacity, which contained an acid solution of hydrogen peroxide. The trap was immersed in boiling water and flushed out with a current of air into the evacuated vessel until atmospheric pressure was reached. The nitrogen dioxide was left for several hours in contact with the hydrogen peroxide solution.

The nitrogen dioxide thus converted to nitrate was determined with 2:4-xylenol, forming the nitro-compound of 2:4-xylenol which is highly colored in alkaline solution (brown). One milliliter of the xylenol reagent was added and the mixture later steam-distilled off, and Nesslerized by comparison with standard color discs.

No attempt was made to correlate the possible bearing of the ozone and nitrogen dioxide content of London air with meteorological conditions. From the results obtained the nitrogen dioxide content of the air in the atmosphere over London was comparable with the amount of ozone present.

#### 1943

PRICE, W. C., "Absorption Spectra and Absorption Coefficients of Atmospheric Gases," *Reports Prog. Phys.* (Phys. Soc., London) 9, 10-17 (1942-1943).

The absorption spectra of  $\text{N}_2\text{O}$ ,  $\text{N}_2\text{O}_3$ ,  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{O}_5$ , and  $\text{NO}_3$  are considered. Statements are made concerning the possibility of their presence in the atmosphere. The abstracts of the report on the above gases are included under the abstract for nitrous oxide ( $\text{N}_2\text{O}$ ), page 36.

SUTHERLAND, G. B. B. M., AND CALLENDAR, G. S., "The Infrared Spectra of Atmospheric Gases Other than Water Vapor," *Reports Prog. Phys.* (Phys. Soc. London) 9, 24 (1942-43).

The authors state that the evidence for the presence of nitrogen pentoxide in the atmosphere is rather weak. The main argument for the presence of  $\text{N}_2\text{O}_5$  in the atmosphere is the reported band at  $7.7\ \mu$ , which later was shown by Hettner, Pohlmann and Schumacher (1934) to be due to  $\text{N}_2\text{O}$ . The ultraviolet spectrum region does not appear to lend support to the presence of atmospheric  $\text{N}_2\text{O}_5$ .

BEYER, KARL, "Determination of Nitrous Gases," *Z. anorg. allgem. Chem.* 250, 321 (1943); *Die Chemie* 56, 14 (1943).

Two methods for the determination of nitrogen dioxide in air are described. The first method consists in absorption in alkaline iodide solution, reducing the nitrate and nitrite formed to  $\text{NH}_3$ , and the subsequent titration of the latter.

The second method involves the photometric determination of  $\text{NO}_2$  by absorption in alkaline solution, and measurement of the color produced by the addition of Ilosvay reagent. The second or colorimetric method permits the determination of low concentrations of  $\text{NO}_2$  and in a much shorter time than the first or titrimetric method.

CHOLAK, JACOB, AND McNARY, ROBERT R., "Determination of the Oxides of Nitrogen in Air," *J. Ind. Hyg. Toxicol.* 25, 354 (1943).

The authors from the Kettering Laboratory of Applied Physiology, College of Medicine, University of Cincinnati, Cincinnati, Ohio have given an excellent discussion of methods for the determination of the oxides of nitrogen in air. Details of five methods are given.

- (1) Phenoldisulfonic Acid Method.
- (2) Diphenylamine Spot Test.
- (3) Chloranil Reaction.
- (4) Titration of Liberated Iodine.
- (5) Polarographic Method.

Comparison of Sensitivity of Methods

Method	mg Nitrate Detected
Polarographic	0.0005/ml solution in polarographic cell
Diphenylamine	0.0025
Phenoldisulfonic acid	0.005
Chloranil	0.025-0.050

PATTY, F. A., AND PETTY, G. M., "Nitrite Field Method for the Determination of Oxides of Nitrogen," *J. Ind. Hyg. Toxicol.* 25, 361 (1943).

The authors utilize the Greiss-Hosvay Reagent (a mixture of sulfanilic acid and alpha naphthylamine) for a field method, and employed sodium nitrate color standards. The method of analysis, instructions for sampling, preparation of color standards, convenience of the method, interfering substances, effects of temperature, accuracy and precision are discussed in detail.

#### 1944

GAYDON, A. G., "Continuous Spectra in Flames: The Role of Atomic Oxygen in Combustion," *Proc. Roy. Soc. (London)* A 183, 111-123 (1944).

The yellow-green air, or so-called oxygen, afterglow, obtained when a discharge is passed through air or through oxygen containing a trace of nitrogen at a pressure of the order of a millimeter of mercury was studied. It was observed that when a very slow stream of nitric oxide is admitted and fairly pure oxygen is used in the discharge, a bright glow was obtained at the point where the gases mix.

The author suggests that the yellow-green continuous spectrum emitted by some flames containing oxides of nitrogen is probably identical with the spectrum of the air afterglow and is due to a reaction between nitric oxide and atomic oxygen. It is stated that the absorption spectrum of the molecule of  $\text{NO}_2$  shows a banded structure in the visible region which would indicate that absorption in this region yields an electronically excited stable  $\text{NO}_2$  molecule. At about 3700 Å the band structure merges into a continuum indicative of the following process.



The reverse process,

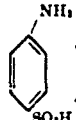
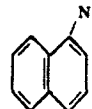


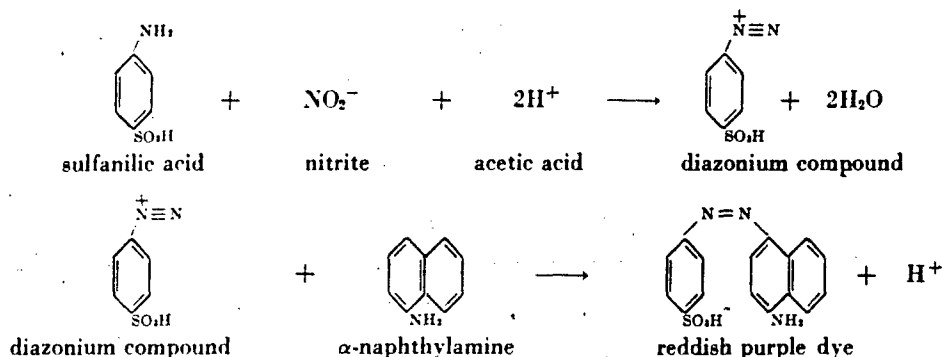
would result in a continuous emission with short-wave limit at about  $\lambda$  3700 Å. If an electron transition probability of the order  $10^7$  or  $10^8$  per sec is assumed, and a duration of the order  $10^{-12}$  or  $10^{-13}$  sec for a collision, the probability for reaction (2) is about  $10^{-5}$  which appears to be of the right magnitude for reaction (2).

1946

RIDER, B. F., AND MELLON, M. G., "Colorimetric Determination of Nitrites," *Ind. Eng. Chem. (Anal. Ed.* 18, 96 (1946)).

This paper describes the authors' experiments upon the use of a General Electric recording spectrophotometer and a Beckman spectrophotometer to determine (a) the effect of reagent concentration, (b) light, (c) nitrite concentration, and (d) the presence of 68 diverse ions on the reddish purple color produced by sulfanilic acid and  $\alpha$ -naphthylamine in the presence of nitrous acid.

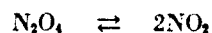
Sulfanilic acid (4-aminobenzenesulfonic acid ) diazotizes nitrous acid, the diazonium compound formed reacts with  $\alpha$ -naphthylamine (1-aminonaphthalene ) to yield a reddish purple colored compound which has its minimum transmittancy near 520 m $\mu$ . The reactions involved are represented as follows:



Reliable determinations can be made by the recommended procedure in the paper in the range of 0.025 to 0.600 parts per million of nitrite ion.

STODDART, E. M., "Effect of Drying on Nitrogen Oxides," *Nature* 157, 702 (1946).

This is an abstract of investigations carried out by Stoddart and reported in full in *J. Chem. Soc.* (1945), pp. 448-451, on the effects of drying the oxides of nitrogen over  $\text{P}_2\text{O}_5$  forming a compound  $\text{P}_2\text{O}_5 \cdot 2\text{NO}$ , thus shifting the equilibrium



to the right in the liquid. The liquid  $\text{N}_2\text{O}_4$  reacts slowly with  $\text{P}_2\text{O}_5$  liberating oxygen causing an increase in pressure.



The dried liquid has a normal vapor pressure, and the results obtained by Stoddart on boiling points, surface tension, liquid density, and dielectric constant show that drying does not influence the physical properties.

## 1947

AVERELL, P. R., HART, W. F., WOODBERRY, N. T., AND BRADLEY, W. R., "Determination of Nitrogen Oxides in Air," *Anal. Chem.* 19, 1040 (1947).

Reference is made to the colorimetric field method for estimating the content of nitrogen oxides in industrial atmospheres by Patty and Petty (1943). The method is based on the hydrolysis of  $\text{NO}_2$  or  $\text{N}_2\text{O}_4$  to nearly equimolecular amounts of nitric and nitrous acids with alpha-naphthylamine, sulfanilic acid, and acetic acid, the nitrite ion reacting to give a red color with the reagent. The disadvantage of the method was that a field kit was necessary to carry a standard fresh nitrite solution to be made up into standards daily.

The authors in the present paper have described the preparation of permanent color standards corresponding to 5 to 50 ppm of  $\text{NO}_2$  in 50 ml of air at  $25^\circ\text{C}$ . The color standards were made from cellophane strips blended with suitable dyes and calibrated by comparison with nitrite standards prepared by the method described by Patty and Petty (1943). The testing procedure is identical to that of Patty and Petty, except the use of the dyed cellophane standards obviates the necessity of preparing color standards from various concentrations of sodium nitrite and the alpha-naphthylamine, sulfanilic acid, acetic acid reagent in the field. The cellophane standards proved to be quite satisfactory for field testing.

DEBIERNE, ANDRE, "The Bikini Cloud," *Compt. rend.* 224, 1220-1222 (1947).

In this paper the author has discussed the presence of the oxides of nitrogen in the atmosphere from atomic bomb explosions. The presence of these oxides is confirmed by the reported color of the cloud. Theoretically 50,000 kg (55 tons) of nitric acid could be produced by one such explosion. The importance of this large amount of acid on meteorological phenomena is considered in the report.

HIEBER, WALTER, "The Structure of the Oxides of Nitrogen," *Sitzber. math-naturw. Abt. bayer-Akad. Wiss. Munchen* (1947), 175 (1949); *Chem. Zentr.* (1950), I, 681.

The authors report that the oxides of nitrogen,  $\text{N}_2\text{O}_3$  and  $\text{N}_2\text{O}_4$ , may be regarded as nitrosyl compounds in which the NO is present as the  $\text{NO}^+$  radical. Thus  $\text{N}_2\text{O}_3$  is considered to be  $(\text{NO}^+)_2\text{O}$  and  $\text{N}_2\text{O}_4$  as  $\text{NO}^+\text{NO}_3$ .

The deep color of nitrogen sesquioxide ( $\text{N}_2\text{O}_3$ ) is explained from this structure and is due to the polarization of the  $\text{O}^-$  ion. Since the  $\text{NO}_3^-$  ion is only slightly polarized, nitrogen tetroxide ( $\text{N}_2\text{O}_4$ ) is colorless.

## 1948

FLAGG, JOHN F., AND LOBENE, RALPH, "A Rapid Method for the Determination of Nitrogen Oxides in Air," *J. Ind. Hyg. Toxicol.* 30, 370 (1948).

Two distinct and different methods for determining nitrogen oxides ( $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{O}_4$ ) in air are available: (1) Oxidation of the oxides to nitric acid using hydrogen peroxide in suitable solution. The nitric acid is then determined by conventional methods, such as diphenylamine, chloranil, phenoldisulfonic acid, or polarographic methods. (2) Absorption of the oxides in a suitable solution, and the determination of the

nitrous acid with alpha naphthylamine sulfanilic acid reagent. Permanent color standards have been developed for this method.

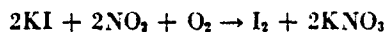
The advantages and disadvantages are given for each method. The method described by the authors in the present paper involves the absorption of the oxides of nitrogen on silica gel, treating with diphenylamine, and comparing the color with standards. The sensitivity is 1-50 ppm (parts per million) of  $\text{NO}_2$ . The advantages claimed for the method are sensitivity, speed, and the requirement of only simple apparatus and reagents. The disadvantage is moderate accuracy.

JOHNSTON, W. S., "Some Methods of Detection and Determination of Gases Encountered Underground," *S. African Ind. Chemist* 2, 107-111 (1948).

In this paper read to the South African Association of Assayers the author from the Geduld Proprietary Mines, Ltd., states that in confined places such as underground workings, small quantities of certain gases may seriously impair the health of the worker. The noxious gases encountered underground are: nitrous fumes  $\text{NO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{HCN}$ ,  $\text{SO}_2$ ,  $\text{CH}_4$ ,  $\text{CO}$ , and  $\text{CO}_2$ .

The Mining Regulations No. 58c and 63b state that no practically detectable traces of the oxides of nitrogen shall be present in either gold or coal mines under the Mine Works and Machinery Regulations. Nitrous fumes may be produced by the burning of low grade cheesa sticks or the detonation or burning of nitroglycerine.

It is stated that nitrous fumes are among the most dangerous gases encountered underground. Exposure to 0.05 percent of  $\text{NO}_2$  for  $\frac{1}{2}$  hour may cause death through bronchitis within 24 hours. The potassium iodide method was employed in the determination of the underground  $\text{NO}_2$ .



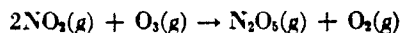
The iodine liberated is estimated by titration with N/10 sodium thiosulfate with starch as indicator.

The sources of the other gases encountered underground, their detection, quantitative determination, and Mining Regulations concerning their presence are discussed in full.

#### 1949

JOHNSTON, HAROLD S., AND YOST, DON M., "The Kinetics of the Rapid Gas Reaction between Ozone and Nitrogen Dioxide," *J. Chem. Phys.* 17, 386 (1949).

This is a study of the kinetics of the fast reaction between ozone and nitrogen dioxide which has been found by Wulf, Daniels, and Karrer (1922) to proceed quantitatively according to the equation



The experimental method, apparatus employed, results of the rate measurements, computations, effects of temperature, and a proposed mechanism to account for the observations are described and discussed in detail. The rate law was found to obey the equation

$$-d(\text{O}_3)/dt = k(\text{NO}_2)(\text{O}_3)$$

for the entire course of the reaction. The energy of activation was found to be  $7.0 \pm 0.6$  kilo-calories per mole. At  $21^\circ\text{C}$  the average value of the rate constant  $k$  is  $3.66 \times 10^7 \text{ cm}^3/\text{mole-sec}$ , the standard deviation for 27 cases was 0.34 in the same units, the standard error of the mean is 0.07.

NORRISH, R. G. W., AND PORTER, G., "Chemical Reactions Produced by Very High Light Intensities," *Nature* 164, 658 (1949).

In this letter to the editor the authors state that it is a matter of general experience that photochemical reactions are not much altered in their courses by change of light intensity. The range of light intensity hitherto available has been limited by that obtainable from the sun and from such sources as high-pressure mercury lamps, the total usable output of which in the region between 2000 and 5000 Å does not exceed  $10^{20}$  quanta second.

A description is given of the gas-discharge flash-lamp which had recently been developed for photographic purposes. The output is described as being continuous down to at least 2000 Å, and appears to be fairly evenly distributed. A table is included which gives the percentage decomposition with a single flash of 4000 Joules lasting less than 2 m sec (meter seconds). The substance is contained in a quartz tube, one meter long, lying parallel to the lamp.

Nitrogen dioxide ( $\text{NO}_2$ ) is one of the substances listed in the table under a pressure of 4 cm Hg,  $\text{NO}_2$  was nearly 100 percent dissociated under the conditions of the experiment.

PEREGUD, E. A., "Gas Analyzer-Colorimeter of Visual Type," *Zavodskaya Lab.* 15, 665 (1949).

The apparatus described in this paper consisted of a small absorption bulb into which the gas sample is introduced from a sample pipette. Nitrogen dioxide is determined by filling the bulb with safranin solution and the color produced is compared visually with a color-concentration scale.

POLESIAEV, N. G., AND GIRINA, V. V., "Determination of Sulfur Dioxide and Nitrogen Dioxide in Air," *Gigiena i Sunit.* (1949), No. 11, 26-29.

Nitrogen dioxide is determined by passing the air sample through an 8 percent solution of potassium iodide, and analyzed colorimetrically by diazotization of sulfanilic acid, coupling with 1-naphthylamine in the presence of sodium sulfite. The color which is developed is compared with standard color samples.

REED, HOMER, REAUGH, MYRL A., AND STRIBLEY, ARTHUR F., JR., "The Petroleum Industry and Smog," *Petroleum Processing* 4, 391 (1949).

Smog is a contraction of the words smoke and fog. It has become a matter of increasing concern in the Los Angeles area. Smog denotes a condition in which natural haze and air contaminants produce a murky atmosphere which sometimes, but not necessarily, causes eye irritation.

As a result of thousands of analytical tests made on a daily basis the following table is included showing the amounts of contaminants in the air in the downtown Los Angeles area.

Contaminant	Usual Concentration ppm
Sulfur dioxide ( $\text{SO}_2$ )	Trace — 0.5
Sulfur trioxide ( $\text{SO}_3$ )	0 — 0.1
Aldehydes	0 — 0.3
Carbon monoxide (CO)	0 — 0.2
Nitrogen oxides ( $\text{NO}$ , $\text{NO}_2$ , $\text{N}_2\text{O}_4$ )	0 — 0.5
Sulfur (elemental)	0 — Trace

The paper is concerned primarily with the amounts of sulfur dioxide released to the atmosphere by refineries.

SCHRENK, H. H., HEIMANN, HARRY, CLAYTON, GEORGE D., GAFER, W. M., AND WEXLER, HARRY, "Air Pollution in Donora, Pennsylvania. Epidemiology of the Unusual Smog Episode of October 1948," U. S. Public Health Bull. No. 306, 173 pp. (1949).

During the last week of October 1948 a heavy smog settled down over the area surrounding Donora, Pennsylvania. Meteorologists described the condition as a temperature inversion and anticyclonic characterized by little or no air movement, prevailing over a wide area of western Pennsylvania, eastern Ohio, and parts of Maryland and Virginia. There was a prolonged stable atmospheric condition accompanied by fog, permitting the accumulation of atmospheric contaminants resulting in dense smog.

The smog encompassed the Donora area on the morning of Wednesday 27 October 1948. The smog continued through Thursday. On Friday a marked increase of illness became prevalent with the result that by Saturday evening 17 persons were dead, while 3 more deaths followed a few days afterward among those who fell ill during the smog.

This study is a detailed report of an investigation by the Division of Industrial Hygiene of the Public Health Service in Washington, D. C. The report comprises 173 pages. The plan of the investigation was (1) to ascertain the cause of the Donora episode, and (2) to obtain information applicable to preventing future occurrences. Three major factors were investigated: (1) The effects on people and animals, (2) Contaminants, and (3) Meteorological conditions.

With reference to the determination of atmospheric contaminants the oxides of nitrogen were determined from atmospheric and stack gas samples. The method employed consisted in absorption in sulfuric acid and hydrogen peroxide. The oxidized nitrogen oxides were determined colorimetrically by the phenol-disulfonic acid method. The color was measured at 410 millimicrons ( $m\mu$ ) by the Coleman spectrophotometer, and the nitrogen concentration read from a standard curve. The following table gives the results of the analyses.

Concentration Range ppm	Number of Samples
0.00-0.19	23
0.20-0.39	3
0.40-0.59	6
0.59 or over	1

The concentrations of the oxides of nitrogen were of a low order of magnitude. In the discussion of the cause of the episode, the concentrations of the oxides of nitrogen found in the atmosphere during the investigation were so small that the possibility was remote that levels accumulated during the October 1948 episode were capable of producing the syndrome observed.

The summary and conclusion of the investigation indicated that the episode in which a total of 5910 persons (42.7 percent) in the Donora area were affected, was not an accidental occurrence but rather resulted from the accumulation of atmospheric pollutants during an unusually prolonged stable air condition. No single substance was responsible, the syndrome could have been produced by a combination, or summation of the action, of several contaminants.

1950

NEILL, H. W., "Atmospheric Phenomena at High Altitudes. Oxides of Nitrogen," University of Michigan, Signal Corps Project 172B, Progress Report No. 17, 14 November 1949 to 13 February 1950, Contract No. M-36-039 sc 32307, page 22 (1950).

The author states that in a survey of the different experimental chemical techniques for the detection and measurement that methods exist for all of the oxides of nitrogen except nitrous oxide ( $N_2O$ ). The technique is incapable of distinguishing between the different oxides,  $NO$ ,  $NO_2$ ,  $N_2O_4$ ,  $N_2O_3$ , or  $N_2O_5$ . A distinction between these oxides would be quite meaningless because of the comparative ease with which they are transformed from one form to another.

Reference is made to the method of converting the oxides to the nitrate and the subsequent detection by one of the following tests (a) chloranil, (b) phenoldisulfonic acid, (c) diphenylamine, and (d) polarographic method. It is pointed out that there are also techniques for the detection of nitrous acid formed by the solution of  $NO_2$  in water. The method involves the use of acetic acid solutions of sulfanilic acid and alpha-naphthylamine (the Greiss-Ilosvay reagent). The acetic acid solution of sulfanilic acid converts the nitrite to a diazo compound which reacts with the alpha-naphthylamine to form a red diazo dye. Reference is made to the adaptation of this technique by Patty and Petty (1943) in devising a micro method for the analysis of  $NO_2$  in small samples of air.

The author describes the adaptation of the method of Patty and Petty to test gas samples of air of the order of 1 ml N.T.P. The method was thoroughly checked for reliability, sensitivity and selectivity by employing various specially prepared gas blends. The author reports the results of the analysis for  $NO_2$  of four rocket samples shown in the table below. There was uncertainty as to the source or the form of these oxides at the time of collection or formation. The following equilibrium equations are given as being of significance.



Results of Analysis for  $NO_2$  from Rocket Samples

Rocket No.	Height of Sampling Km	Analysis by Volume ppm
A P L V-2 #35	55.4-65.5	83
A P L V-2 #40	49.0-59.8	180
Aerobee SC-2	49.6-53.6	480
Aerobee SC-3	47.0-50.4	60

OGG, RICHARD A., JR., "Nitrogen Pentoxide Formation in the Oxygen-Nitric Oxide Reaction," *J. Chem. Phys.* 18, 770 (1950).

The author states that the standard free energy change of the reaction,



may be found from the well-known thermodynamic properties of  $NO$  and  $O_2$  together with the heat of formation of  $N_2O_6$ .

From previous kinetic considerations it had been suspected that under proper conditions the rate of reaction (1) might be significant in the rate of the reaction



which previously had been considered the sole process of the oxygen-nitric oxide system. The following proposed mechanism is given for reaction (1).



It was concluded from the results of the experiments in this investigation that  $\text{N}_2\text{O}_5$ , unequivocally, is formed in significant amounts. A brief description of the experimental method, and a discussion of the data obtained are included.

WADE, HARLAND A., ELKINS, HERVEY B., AND RUTOLO, BENJAMIN P. W., "Composition of Nitrous Fumes from Industrial Processes," *Arch. Ind. Hyg. Occupational Med.* 1, 81 (1950).

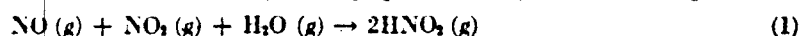
The authors state that of the toxic gases occurring in industry which occasionally jeopardize the public, the oxides of nitrogen are among the most dangerous. Reference is made to the Cleveland Clinic film disaster in 1929 in which 125 deaths resulted due to the inhalation of these fumes.

The following topics are considered in the report: (1) Chemistry of nitrous fumes. (2) Toxicologic observations. (3) Laboratory experiments. (4) Composition of nitrous fumes unabsorbed by silica gel. (5) Field experiments where studies were made in eleven establishments of nitrous fumes given off in actual industrial processes. (6) Permissible concentration for nitrous fumes.

The authors report a method for the separate determination of the nitric oxide and the nitrogen dioxide in the air, based on the fact that  $\text{NO}_2$  is absorbed by silica gel. The efficiency is approximately 80 percent, and the 20 percent not absorbed is largely converted to nitric oxide.

WAYNE, LOWELL C., AND YOST, DON M., "Rate of the Rapid Gas Phase Reaction between  $\text{NO}$ ,  $\text{NO}_2$  and  $\text{H}_2\text{O}$ ," *J. Chem. Phys.* 18, 767 (1950).

In this study the authors have used the cathode-ray oscillograph to investigate the following reaction,



which the authors suggest is probably involved in the atmosphere immediately after a lightning stroke. One hundred and twenty-three separate runs were made at temperatures from 23° to 25°C.

Employing a constant large excess pressure of  $\text{NO}$  (1 atmos) the ratio between the concentrations of the molecular species  $\text{NO}$  and  $\text{N}_2\text{O}_5$  was kept constant at 2.1. The initial partial pressure of  $\text{NO}_2 (g)$  was varied from 0.005 to 0.03 atmos, the  $\text{H}_2\text{O} (g)$  between 0.09 and 0.025 and the molecular ratio of  $\text{NO}_2$  to  $\text{H}_2\text{O}$  between 0.34 and 2.5.

The general differential rate equation was written as

$$dx/dt = Y[(a - x/2)(b - x/2) - x^2/K] \quad (2)$$

where  $x$  denotes  $P_{\text{HNO}_2}$ ,  $a$  and  $b$  are initial values of  $P_{\text{NO}}$  and  $P_{\text{H}_2\text{O}}$ , respectively,  $k$  is the rate constant of reaction (1), and  $K$  the appropriate equilibrium constant,  $Y$  is a factor to represent any catalytic or inhibitory influences affecting the rate. The rate constant  $k$  was estimated at  $7.3 \times 10^4 \text{ atmos}^{-2} \text{ sec}^{-1}$ .

1951

CARRINGTON, TUCKER, AND DAVIDSON, NORMAN, "Photoelectric Observation of the Rate of Dissociation of  $N_2O_4$  by a Shock Wave." *J. Chem. Phys.* 19, 1313 (1951).

The rates of the very fast reaction,



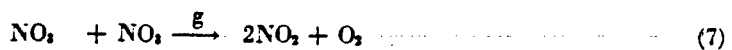
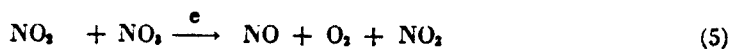
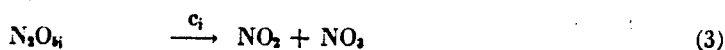
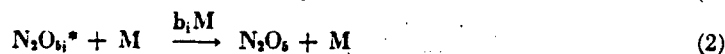
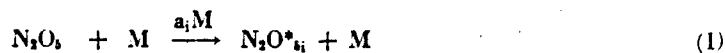
is of special interest in connection with the study of the dispersion of sound velocity in a dissociating gas (Einstein, *Sitzber. preuss. Akad. Wiss.*, 380 (1920)).

The principle of the method described in this letter to the editor involves a rapid compression and heating of the equilibrium mixture,  $NO_2$ ,  $N_2O_4$ , the subsequent dissociation of  $N_2O_4$  is then followed by fast photoelectric techniques. A detailed description is given of a typical experiment. Precise measurements of the shock velocity, and of the shock temperature and pressure had not yet been made. Preliminary experiments gave a unimolecular rate constant for the dissociation of  $N_2O_4$  of  $1 \times 10^5 \text{ sec}^{-1}$ , at  $25^\circ\text{C}$  and 1 atmos of  $N_2$ .

JOHNSTON, HAROLD S., "Four Mechanisms Involving Nitrogen Pentoxide," *J. Am. Chem. Soc.* 73, 4542 (1951).

Four complex kinetic systems involving  $N_2O_5$  are given in this report. These can be expressed in terms of eight processes. The four mechanisms are: (1) The decomposition of nitrogen pentoxide, (2) the decomposition of nitrogen pentoxide in the presence of nitric oxide, (3) the decomposition of ozone in the presence of nitrogen pentoxide, and (4) the formation of nitrogen pentoxide from ozone and nitrogen dioxide.

The eight reaction processes are:



LARSON, GORDON P., "Second Technical and Administrative Report on Air Pollution Control in Los Angeles County" (1950-51).

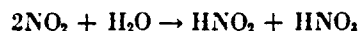
The report is subdivided into ten sections as follows:

- I. Why Los Angeles County has Smog.
- II. How Smog Affects Us.
- III. What Contaminates the Air.

- IV. How Smog is Controlled.
- V. Administration.
- VI. Analysis of the Los Angeles Atmosphere.
- VII. Chemical and Physical Properties of Los Angeles Smog.
- VIII. Total Daily Emissions to the Los Angeles Atmosphere.
- IX. Reduction in Pollution Levels.
- X. Effects of Los Angeles Smog on Vegetation.

In answering the question why Los Angeles has smog, it is stated that the air which normally reaches the California coast, particularly in summer, comes clockwise around a large high pressure area lying over the Pacific Ocean with its center north of Hawaii. As the column of air moves southeastward around this "high," the upper portion sinks and is heated by compression. The air next to the ocean surface is cooled from below. This produces a layer of cold, moist layer below the warm, dry, descending layer. This condition is known as a temperature inversion, with warm air above a layer of cold air.

In section VI, Analysis of the Los Angeles Atmosphere, a brief discussion is given about the oxides of nitrogen in the atmosphere, nitrogen dioxide ( $\text{NO}_2$ ) being the most prevalent. The following reaction occurs when  $\text{NO}_2$  is dissolved in an alkaline medium.



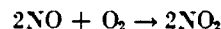
Since an equimolecular mixture of nitrite and nitrate is formed, the method used for analysis consists in determining the amount of nitrous acid, and multiplying by a factor of two in order to calculate the total amount of oxides of nitrogen.

The method employed in the laboratory was based on the Griess-Ilosvay reaction for the determination of nitrites. The sulfanilic acid reacts with nitrous acid yielding a diazonium salt which when coupled with alpha-naphthylamine produces a pink color. A colorimeter is used to measure the intensity of the color, and hence the amount of nitrite.

In section VII, the Chemical and Physical Properties of Los Angeles Smog is considered. With reference to the role of  $\text{NO}_2$ , the absorption of solar energy leads to the photodissociation of the  $\text{NO}_2$  molecule into nitric oxide ( $\text{NO}$ ) and atomic oxygen ( $\text{O}$ ).



The nitric oxide combines with molecular oxygen and regenerates the



original nitrogen dioxide molecule. In this respect  $\text{NO}_2$  is considered as a catalyst, available for an indefinite number of such cycles. The atomic oxygen formed during the cycle is able to react with organic compounds and molecular oxygen yielding complex intermediate peroxide compounds and ozone, producing the oxidizing properties of Los Angeles air.

MATHESON, DELOSS H., "Inorganic Nitrogen in Precipitation and Atmospheric Sediments," *Can. J. Technol.* 29, 406-412 (1951).

This investigation extended over a period of 18 months starting in January 1949. Daily determinations were made of the inorganic nitrogen contained in precipitation and atmospheric sediments collected at Hamilton, Ontario.



The experimental method is described. The nitrogen content was determined as ammonia, and as nitrate by the regular chemical methods for the analysis of these nitrogen compounds. Several summarizing tables of the results are included. It was found that significant amounts of inorganic nitrogen compounds are contributed to soil and the surface of bodies of water by the deposit of precipitation and atmospheric sediments.

During the last six months of 1949, 249 milligrams of nitrogen per square meter were collected. This is equivalent to 5.2 lb per acre per year. The collections for the year 1950 totaled 6.2 lb per acre per year. Of this amount of total nitrogen an average of 56 percent was ammonia nitrogen.

SHEPHERD, MARTIN, AND ROCK, S. M., HOWARD, ROYCE, AND STORMES, JOHN, "Isolation, Identification, and Estimation of Gaseous Pollutants of Air," *Anal. Chem.* 23, 1431 (1951).

The authors from the National Bureau of Standards, Washington, D. C., and the Consolidated Engineering Corporation, Pasadena, California have described the use of the mass spectrometer in the examination and identification of gaseous pollutants of air in smog. Three essential steps are outlined: (1) Isolation of the gaseous pollutants from the air on a filter at the temperature of liquid oxygen. (2) Separation of the isolated concentrate by isothermal distillation or sublimation at low temperatures and pressures. (3) Immediate analysis of the distillate with the mass spectrometer.

Each of these steps is thoroughly described in detail. Nitrous oxide was identified from peaks 30 and 41. The method has a sensitivity of  $10^{-4}$  ppm of some pollutants from a 100-liter sample of air, and with larger samples  $10^{-5}$  ppm of some substances can be determined.

The gaseous phase of the smog was found to be of the order of 0.5 ppm of Los Angeles air. The most important of some 60 chemical compounds identified in the smog were the oxidized unsaturated hydrocarbons, oxidized with ozone and nitrogen dioxide in the presence of sunlight, producing substances which constitute a large proportion of smog concentrates. These oxidation products cause eye and respiratory irritation. The results of the present paper support the evidence obtained by Haagen-Smit (1951) that the presence of peroxides in particulate matter characterize the damaging components in smog.

#### 1952

BLACET, F. E., "Photochemistry in the Lower Atmosphere," *Ind. Eng. Chem.* 44, 1339-1342 (1952).

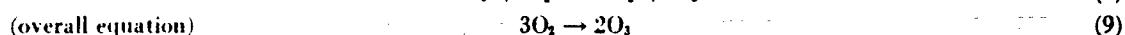
This is a paper presented at the Symposium on Air Pollution at the XII International Congress of Pure and Applied Chemistry, New York, September 1951. A brief resume is given of the oxygen role in the upper atmosphere in the formation of ozone. The following mechanism is given as a possible way in which ozone may be formed in the lower atmosphere as a by-product of the photolysis of sulfur dioxide.



With reference to the oxides of nitrogen it is stated that they are to be expected as combustion products in industrial areas. The oxides of nitrogen have been found in Los Angeles atmosphere in concentrations comparable for sulfur dioxide (Annual Report, 1949-1950, Air Pollution Control District County of Los Angeles, California).

The author in the present paper states that nitrogen dioxide ( $\text{NO}_2$ ) may be regarded as the most prevalent of the oxides of nitrogen in air pollution. Nitrogen dioxide absorbs radiation from 6000 Å down to well below 2000 Å. From 6000 to 3700 Å it is stated that the spectrum indicates only the formation of excited molecules, and the dissociation quantum yield is low. However, below 3700 Å the absorption bands are diffuse and the primary quantum efficiency of dissociation is near unity (Dickinson, R. G., and Baxter, W. P., *J. Am. Chem. Soc.* 50, 774 (1928); Holmes, H. H., and Daniels, F., *J. Am. Chem. Soc.* 56, 6307 (1934)).

The following speculative mechanism is given where the oxygen-nitrogen dioxide ratio is very large.



These postulated steps are reasonable and indicate a way in which nitrogen dioxide may serve as an intermediate in making solar radiation available for use in the formation of atmospheric ozone from oxygen. In equation (8)  $\text{NO}_2$  is regenerated and therefore available to repeat the process. Nitrogen dioxide may be more effective than sulfur dioxide in forming ozone in the lower atmosphere, (a) because of a much higher primary quantum efficiency, and (b) because of its catalytic effect, sulfur dioxide not being regenerated in the above mechanism for ozone formation from the photolysis of  $\text{SO}_2$ .

It is pointed out that these reactions occur in the lower atmosphere while none of the high altitude photochemical reactions can occur in the lower atmosphere. The photochemical reactions which occur in the lower atmosphere are initiated as a result of sunlight absorption by atmospheric pollutants produced primarily in industrial processes. The formation of ozone by the catalytic action of nitrogen dioxide may prove to be the most significant.

An excellent bibliography of twenty references is included. The list includes such names as: S. Chapman, C. H. Bamford, R. Penndorf, O. R. Wulf, C. Fabry, and others.

GRAY, EDWARD LEB., MACNAMEE, JAMES K. AND GOLDBERG, STANLEY B. "Toxicity of  $\text{NO}_2$  Vapors at very Low Levels," *Arch. Ind. Hyg. Occupational Med.* 6, 20 (1952).

The opinions of various workers differ greatly as to the toxic levels of  $\text{NO}_2$  vapors, particularly for chronic exposures at low levels. There is also a great divergence of values for the maximum allowable concentrations.

The value set by the American Standards Association and others is 25 ppm (parts per million). The authors point out the risk involved in translating experiments on animals to conditions encountered by humans. It is stated that amounts of  $\text{NO}_2$  over 8 ppm produce damage in rats and may cause injury to man. In the opinion of the authors a maximum allowable concentration of 25 ppm or more is too high. This is a preliminary study by workers at the Army Chemical Center, Maryland.

HAAGEN-SMIT, A. J., "Chemistry and Physiology of Los Angeles Smog," *Ind. Eng. Chem.* 44, 1342 (1952).

In this paper the author states that under the influence of sunlight, nitrogen dioxide dissociating into nitric oxide and atomic oxygen readily oxidizes a number of compounds. Nitric oxide is oxidized by molec-

ular oxygen to nitrogen dioxide, thus functioning as a continuous source of atomic oxygen. In the Los Angeles area the nitrogen dioxide concentration reaches values of 0.4 parts per million.

Laboratory experiments employing this value, 0.4 ppm of nitrogen dioxide and hydrocarbons derived from gasoline gave intermediate peroxide compounds formed in the presence of sunlight, which are responsible for typical plant damage. With reference to eye irritation it was observed that when a cracked gasoline was released in the presence of nitrogen oxides and sunlight, the characteristic odor and eye irritation soon became apparent.

With the aid of the mass spectrograph valuable information was obtained on the multitude of hydrocarbons present in Los Angeles air. The mass spectrograms also showed the presence of similar compounds in smog as those produced from mixtures of hydrocarbons, oxidized with ozone, nitrogen oxides, and ultraviolet light. Estimates show that from combustion processes that nitrogen oxides are liberated at a rate of 200 to 300 tons daily into the Los Angeles air.

The author gives the Schematic Presentation of Reactions in Polluted Air leading to Smog Symptoms as shown on page 45 in the summary and evaluation of this survey.

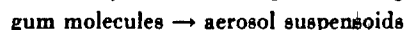
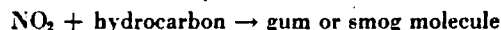
HALL, EDWIN L., "What is the Role of the Gas Industry in Air Pollution?" *Gas* 28, No. 10, 54 (1952).

Reference is made to the investigations of A. J. Haagen-Smit (*Eng. and Sci.*, December 1950) and Shepherd and co-workers (*Anal. Chem.*, October 1951) who showed that in the presence of sunlight oxides of nitrogen and hydrocarbons will produce crop damage, eye irritation and rubber cracking. It was shown that vapor phase gum would not be formed in sufficient quantities to cause trouble if the reaction,



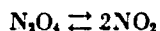
was not catalyzed by certain conjugated diolefins, such as butadiene and cyclopentadiene, which are normally present in manufactured gas.

The following sequence reactions are given:

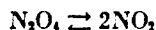


HALL, T. C., AND BLACET, F. E. "Separation of the Absorption Spectra of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  in the Range 2400-5000 Å," *J. Chem. Phys.* 20, 1745-1749 (1952).

The effect of a thermal equilibrium shift on the



absorption is discussed. As the temperature is raised the increase of  $\text{NO}_2$  and decrease of  $\text{N}_2\text{O}_4$  concentration in the range 2400-2900 Å was evident. The increased probability of the  $\text{N}_2\text{O}_4$  rather than the  $\text{NO}_2$  absorbing incident radiation as the wavelength is decreased is of photochemical interest. The quantum yield data for systems containing



should be a function of the ratio  $p_2/p_1$ , and hence to total pressure  $p_1$ . Reduction of the wavelength of incident light over a sufficient range could change the primary absorber from  $\text{NO}_2$  to  $\text{N}_2\text{O}_4$ , and as a result alter the photochemistry of the system.

Involved in the study was the calculation of the absorption coefficients of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  from the optical density curves ( $\log I_0/I$ ) of the mixture under conditions of different total pressure where the ratios of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  are different. The continuous calculation of the absorption coefficients over the range of wavelengths was accomplished by means of a mechanical analog differential analyzer. The experimental method is described as well as the calculations and errors.

MCCABE, LOUIS C., "Air Pollution," McGraw-Hill Book Company, Inc., New York (1952), pp. 151 and 651.

In chapter 15 of this excellent book on the Proceedings of the U. S. Technical Conference on Air Pollution, H. F. Johnstone of the University of Illinois has discussed the Properties and Behavior of Air Contaminants. With respect to the nitrogen oxides,  $\text{NO}$  and  $\text{NO}_2$ , the threshold concentration value is 25 parts per million by volume. The dangerous or fatal concentration value is 100–150 parts per million. The physiological effects are irritation and edema.

The oxides of nitrogen are seldom found in air in concentrations to the extent that their physiological effects can be noticed. Concentrations as high as 0.4 ppm have been reported in the Los Angeles atmosphere. The oxides of nitrogen may contribute indirectly to air pollution by catalyzing the oxidation of  $\text{SO}_2$ . Thus they are responsible in part for the acidity in rain and fog and hence are factors to atmospheric corrosion.

The oxides of nitrogen are by-products of the combustion of some kinds of fuels, particularly by oxidation of ammonia waste gases from refineries which employ the regeneration of cracking catalysts, sulfuric acid manufacturing plants, and pickling processes for stainless steels are all sources of the oxides of nitrogen to air pollution.

In chapter 17 Clelio Brunetti, P. L. Magill, and F. G. Sawyer of the Stanford Research Institute, Stanford, California have discussed new developments in instrumentation for air pollution studies. The oxides of nitrogen are collected by scrubbing 50 cubic feet of air with 50 milliliters of 5 percent sodium hydroxide solution. After oxidation of the oxides of nitrogen in solution by hydrogen peroxide they are determined colorimetrically by using phenolsulfonic acid reagent. The sensitivity of this method is 0.05 ppm with an accuracy of 10 percent.

#### 1953

HAAGEN-SMIT, A. J., BRADLEY, C. E. AND FOX, M. M. "Ozone Formation in Photochemical Oxidation of Organic Substances," *Ind. Eng. Chem.* 45, 2086 (1953).

The authors state that smog periods in the Los Angeles area are chemically characterized by a pronounced oxidizing effect, of the order of 0.6 ppm calculated as hydrogen peroxide usually determined by the liberation of iodine from neutral buffered potassium iodide solution. Another method for measuring the oxidizing action of smog consists in the coloration of dyes such as indigo sulfonic acid or crystal violet. A convenient smog indicator is colorless phenolphthalein, which is oxidized to phenolphthalein (red in alkaline solution). The intensity of the red color is a direct measure of the smog concentration.

The oxidizing effect of smog has been shown to be due to the combined action of nitrogen oxides, peroxides, and ozone, counteracted by the reducing action of sulfur dioxide (0.1 to 0.2 ppm). The presence of peroxides in the atmosphere is explained by the photochemical oxidation of hydrocarbons liberated into the air. Nitrogen oxides function as catalysts in the formation of these peroxides. The natural ozone concentration on the earth's surface is reported to be approximately 0.02 to 0.03 ppm.

The experiments reported in the present paper were designed to study the formation of ozone through photochemical reactions in the presence of oxides of nitrogen and various organic substances. It was demonstrated that ozone was formed through photochemical oxidation of alcohols, aldehydes, ketones, acids, and hydrocarbons, such as are present in gasoline in the presence of small concentrations of the oxides of nitrogen.

The ozone formation was attributed to a peroxide radical chain reaction. It was shown from the experiments which the authors conducted that the release of large quantities of hydrocarbons into the air simultaneously in the presence of oxides of nitrogen from combustion processes explains the relatively high ozone concentration in the Los Angeles area. The effects are of economic consequence and health hazards.

The photochemical dissociation of nitrogen dioxide in the presence of sunlight provides a continuous source of atomic oxygen. The regeneration of nitrogen dioxide by oxidation of the nitric oxide causes the reaction to be continuous. The ozone content during smog periods has repeatedly been determined to be from 0.2 to 0.3 ppm which are several times the maximum level (0.1 ppm) recommended by the American Medical Association Council on Physical Therapy for safe working conditions.

LARSON, GORDON P., FISCHER, GEORGE L., AND HAMMING, WALTER J., "Evaluating Sources of Air Pollution," *Ind. Eng. Chem.* 45, 1070 (1953).

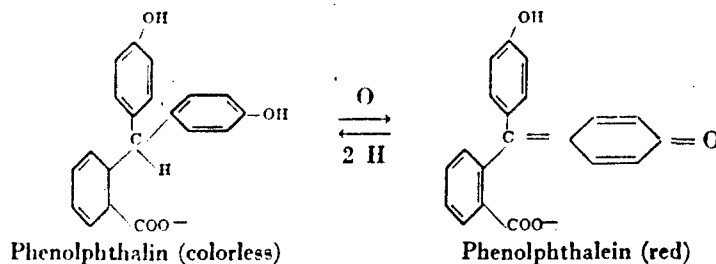
The concentration of the oxides of nitrogen in the atmosphere over downtown Los Angeles, California has been determined on various days during 1951. The following correlation was noted for periods of good visibility and during periods of intense smog.

	Periods of Good Visibility (7 miles)	Periods of Intense Smog
Concentration of Oxides of Nitrogen	ppm 0.08	ppm 0.4

MCCABE, LOUIS C., "Atmospheric Pollution," *Ind. Eng. Chem.* 45, 111 A (1953) (September number).

In this monthly column McCabe has discussed a method for estimating oxidant in the air. The method is based on the oxidation of phenolphthalin to phenolphthalein. Reference is made to the importance of ozone, peroxides, and oxides of nitrogen in the formation of air contaminants which has been described by Haagen-Smit (*Ind. Eng. Chem.* 44, 1342 (1952)), and by Littman and Magill ("Some Unique Aspects of Air Pollution in Los Angeles," Standard Research Institute (1953)).

The oxidation-reduction of phenolphthalin is illustrated by structural formulas in the following reaction:



The author reports that the Beckman Instruments Inc. of South Pasadena, California is now building an instrument for the determination of total oxidant in the air. The method is based upon the oxidation of phenolphthalin to phenolphthalein which provides a sensitivity of less than 1 ppm oxidant in the air. The preparation of the phenolphthalin test reagent, testing procedure, the use of the Klett-Summerson colorimeter followed by estimation from a standard curve are described.

MOORE, GORDON E., "The Spectrum of Nitrogen Dioxide in the 1.4-3.4  $\mu$  Region and the Vibrational and Rotational Constants of the  $\text{NO}_2$  Molecule," *J. Opt. Soc. Am.* 43, 1045 (1953).

The spectrum of  $\text{NO}_2$  was observed with a vacuum grating spectrograph using PbS and PbTe photoconducting detectors. The observation cells employed were 100, 120 and 200 cm in length. The experimental details are given. Nine absorption bands were observed and the frequencies of the band centers of  $\text{NO}_2$  are listed. The fundamental frequencies of  $\text{NO}_2$  are given:  $\nu_1 = 1322.5 \text{ cm}^{-1}$ ,  $\nu_2 = 750.9 \text{ cm}^{-1}$ , and  $\nu_3 = 1616.0 \text{ cm}^{-1}$ . All nine bands reported in this investigation had rotational structure at least partially resolved. Two apparently abnormal interactions occur between vibrational lines  $3 \nu_3$  and  $2 \nu_1 + 3 \nu_2$ , and between  $\nu_1 + 3 \nu_3$  and  $3 \nu_1 + 3 \nu_2$ .

The structural ground state parameters are:

$$r_{\text{N-O}} = 1.188 \pm 0.004 \text{ \AA} \text{ and } \angle \text{O-N-O} = 134^\circ 4' \pm 15'$$

which are in close agreement with electron diffraction data

$$r_{\text{N-O}} = 1.20 \pm 0.02 \text{ \AA}, \text{ and } \angle \text{O-N-O} = 132^\circ \pm 3^\circ.$$

NICOLET, MARCEL, "Aeronomical Problems of Nitrogen Oxides," Ionospheric Research, Scientific Report No. 52, The Pennsylvania State College, 25 October 1953, AMC Contract No. AF19(122)-44.

In this report Nicolet has considered the photochemistry of nitrogen dioxide in the upper atmosphere along with (a) nitrous oxide and (b) nitric oxide which generally are regarded to be the most important of the oxides of nitrogen at high levels and in ionospheric phenomena.

Nitrogen dioxide is not considered an important constituent in the mesosphere during daylight, since the rate coefficient of dissociation is high. Nitrogen dioxide processes during the night have not been investigated; however laboratory studies indicate many interesting phenomena. Reference is made to the fluorescence which occurs in two visible bands lying in the red-orange (6200-6300  $\text{\AA}$ ) and the yellow-green (5600-6050  $\text{\AA}$ ) parts of the spectrum observed by Norrish (1929) and by Baxter (1930). Also Gaydon (1944) has reported the formation of  $\text{NO}_2$  by a radiative process involving nitric oxide and atomic oxygen as a process leading to an emission spectrum.

Several laboratory investigations on radiative processes indicate that nitrogen dioxide may be an important contributor to the continuous airglow spectrum. Nitrogen dioxide and atmospheric oxygen system is discussed in the light of data found by Bodenstein and Linderer (1929), Holmes and Daniels (1934), Hall and Blacett (1952), and others.

From a study of nitrogen dioxide formation and photodissociation



it was observed that the ratio  $n(\text{NO}_2)/n(\text{NO}) \ll 1$  has no practical effect on the nitric oxide day concentration; however the ratio varies very rapidly and is different during day and night. The photodissociation rate coefficient (about  $5 \times 10^{-3} \text{ sec}^{-1}$ , Bates (1952)) is necessary to consider in the D region reactions.

The author states that the photoionization of nitrogen dioxide is so rapid during the day that its action on the nitric oxide concentration can be neglected. The night mechanisms are the following:



about  $10^{-17} \text{ cm}^3 \text{ sec}^{-1}$ , Bates (1952).



The following differential equation involving processes affecting  $\text{NO}_2$  was suggested.

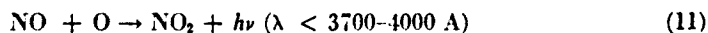
$$\frac{dn(\text{NO}_2)}{dt} = b_3 n(\text{NO}) n(\text{O}) + b_1 n(\text{NO}) n(\text{O}_3) - b_2 n(\text{NO}_2) n(\text{O}) - (\text{NO}_2) J_{\text{NO}_2} \quad (9)$$

From theoretical calculations Nicolet concluded that the transformation of  $\text{NO}$  into  $\text{NO}_2$  during the night is important in the entire mesosphere. The nitric oxide ( $\text{NO}$ ) taken as about  $10^8 \text{ cm}^{-3}$  near 80 km would be of the order of  $10^9 \text{ cm}^{-3}$  at 65 km, the  $\text{NO}_2$  nocturnal concentration could be represented by values of about the same orders of magnitude or less, the  $\text{NO}_2$  concentration being limited by the day concentration of  $\text{NO}$  in the entire mesosphere.

With reference to the night airglow Nicolet states that the reaction between  $\text{NO}_2$  with  $\text{O}$  is an important process that cannot be neglected.



The bi-molecular association,



is suggested as corresponding to the continuous airglow observed by Rayleigh (1910) and later studied by Stoddart (1934) and Newmann (1935) in more detail, indicating reaction mechanism (11) to be important. The mechanism,



is also considered as a process in the night airglow.

#### 1954

MORI, K., "The Absorption Spectrum of Nitrogen Dioxide in the Vacuum Ultraviolet," *Science of Light* (Tokyo) 3, No. 1, 62 (1954).

The band spectra of nitrogen dioxide ( $\text{NO}_2$ ) were photographed in the vacuum ultraviolet. The spectral region  $\lambda$  1600–1350 Å could be considered as a combination of two progressions, one having a frequency of about  $400 \text{ cm}^{-1}$ , and the other  $600 \text{ cm}^{-1}$ . Fifteen new diffuse bands were found at about  $\lambda$  1800 Å. The author concludes that the electronic structure of  $\text{NO}_2$  suggested by his investigations is in agreement with that predicted earlier by Mulliken.

SALTZMAN, BERNARD E., "Colorimetric Microdetermination of Nitrogen Dioxide in the Atmosphere," *Anal. Chem.* 26, 1949 (1954).

The toxicity of nitrogen dioxide is emphasized. A concentration of five parts per million of nitrogen dioxide is the maximum safe allowance. This gas is liberated during many operations, such as explosives, welding operations, exhaust of internal combustion engines, and in chemical processes involving nitration. Some of the difficulties in the past have been: absorbing the gas from a sufficiently large sample, uncertainty of results for levels below 5 ppm, collection in large bottles for the well-known phenoldisulfonic acid method, length of time required for complete analysis.

In the present paper the author has reported the development of a reagent which is specific for nitrogen dioxide, and can be used for continuous sampling. The reagent is a mixture of sulfanilic acid, N-(1-naphthyl)-ethylenediamine dihydrochloride, and acetic acid. The sensitivity claimed is a few parts per billion for a 10-minute sample at 0.4 liter per minute. The apparatus includes a Beckman Model D U spectrophotometer, midget fritted bubblers, and grab-sample bottles. The reagents employed are stable for several months if kept stored in a refrigerator in well stoppered brown bottles. The reagents are: (a) N-(1-naphthyl)-ethylenediamine dihydrochloride, (b) Absorbing reagent of sulfanilic acid in glacial acetic acid, and (c) Standard sodium nitrite solution.

The preparation of the reagents, the procedures for sampling, standardization determination, and calculations are described in detail. The effects of the various interfering gases are considered and found to be unimportant.

MUKHERJEE, ASOKE KUMAR, "Thunderstorm and Fixation of Nitrogen in Rain," *Indian J. Meteorol. Geophys.* 6, 57 (1955).

The author in the present paper has reviewed the recent determinations of nitrate and ammonia in rain water in Sweden. The results of these analyses led to the conclusion that thunder (electrical spark discharges in the atmosphere) was not a determining factor in the production of nitrogen compounds formed in rain water.

As a result of the data obtained in Sweden the present investigation of combined nitrogen in rain water in India was undertaken. It was concluded that the mechanism of the formation of nitrates in the atmosphere is quite complicated. The electric spark discharge may have some effect in the lower atmosphere, but it cannot be considered primarily responsible for the formation of nitrates in rain.

The author is in agreement with Virtanen (1952) that the determination of nitrogen compounds at different altitudes is indispensable in obtaining information of the nitrogen fixation in the atmosphere. A bibliography of eight references to previous studies of nitrogen fixation in the atmosphere is included.

NICOLET, MARCEL, "The Aeronomic Problem of Nitrogen Oxides," *J. Atm. Terrest. Phys.* 7, 152 (1955).

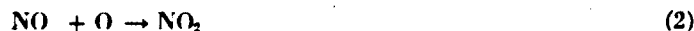
In this theoretical analysis of the aeronomy of nitrogen oxides the author considers nitrogen dioxide ( $\text{NO}_2$ ) as an atmospheric constituent. During daytime this oxide of nitrogen cannot be considered important in the mesosphere since the dissociation rate coefficient is high. Reference is made to the spectroscopic studies of  $\text{NO}_2$  by Norrish (1929), by Baxter (1930), Gaydon (1944), Rayleigh (1910), Stoddard (1934), Newman (1935), Spealman and Rodebush (1935), Kondratjew (1936), and by Tanaka and Shimazu (1948).



The author states that the formation of  $\text{NO}_2$  during the night is a problem that remains to be investigated. The reaction



may be important at night. From a study of  $\text{NO}_2$  formation and photodissociation



the ratio  $n(\text{NO}_2)/n(\text{NO}) \ll 1$ .

It is concluded that there is no effect of the daytime nitric oxide (NO) concentration. Atmospheric mixing is considered to be of practical importance in fixing the vertical distribution of nitric oxide more than a vertical distribution by photochemical equilibrium. The ratio  $n(\text{NO}_2)/n(\text{NO})$  is shown to vary rapidly and is different during the day and night. The essential night-time mechanisms for  $\text{NO}_2$  are



for which Bates (1954) gives the rate coefficient of about  $10^{-17} \text{ cm}^3 \text{ sec}^{-1}$ .



In the latter reaction the rate coefficient depends on the activation chosen. During night the equilibrium ratio,  $n(\text{NO}_2)/n(\text{NO})$  is greater than one in the ozone region. At 90 km where oxygen atoms are involved the ratio is considered less than unity.

In regard to the abundance and distribution of nitric oxide (NO) molecules in the mesosphere, Nicolet states that as a first approximation the distribution follows atmospheric vertical distribution. It is concluded that the concentration of nitric oxide cannot be more than  $10^{11} \text{ cm}^{-3}$  at 80 km.

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